Spring 5-31-1989

Microwave treatment of organic contaminated soil

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ABSTRACT

The development of microwave technology to treat hazardous wastes has been in progress at NJIT for the past three years. The initial stages of this program have focused on determining the breadth of hazardous waste problems that are amenable to microwave technology applications. Benchscale studies have shown the following processes are technically possible:

a. It is possible to steam strip organic volatiles from soil;
b. Volatiles can be destroyed by impact upon "lossy" solids;
c. Heavy metal ions can be immobilized in soil;
d. It is possible to regenerate GAC on-site.
e. It is possible to pyrolyze polyarmotic compounds in soil in-site, and, thereby, effect decontamination.

In this thesis, it has been shown that a relatively non-volatile compound like naphthalene can be steam-stripped from soil; that the incident microwave energy penetrates the soil; that for volatile compounds are difficult to quantify effects; that in a comparison of microwave to incineration based upon economic and other considerations. It is concluded that microwave can play an potentially significant role in the clean up at contaminated soil.

MICROWAVE TREATMENT
OF
ORGANIC CONTAMINATED SOIL

BY

SUNING FAN

Thesis submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
Master of Science in Environmental Science

1989

APPROVAL SHEET

Title of Thesis: Microwave Treatment of Organic Contaminated Soil

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Title of Thesis: Microwave Treatment of Organic-Contaminated Soil

Suning Fan, Master of Environmental Science, 1989

Thesis directed by: Professor of the Department of Chemical
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The author of this thesis would like to extend special thanks to Dr. Leonard Dauerman and his research associate, Ms. Gabriele Windgasse.

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Other work in progress in this laboratory include: a) the installation of a pilot plant; b) the setting up of a full scale plant in the Raytheon Inc. facility in Waltham, MA; c) the destruction of non-volatile organics in soil; d) the determination of the atomic mechanism underlying the immobilization of heavy metals in soil.

OBJECTIVE

The main objective of this thesis is to study the application of microwave technology to the steam stripping of a relatively non-volatile organic from soil. The subordinate objective is to analyze the potential of microwave technology to either displace or, more likely, to supplement rotary kiln incineration as a method of treating soil contaminated with volatilizable organics.

The soil contaminated studied was naphthalene, which is a solid at room temperature with a measurable vapor pressure; thus, it is regarded as a relatively non-volatile organic. Other studies were carried out on trichlorethylene which is a volatile organic compound.

CHAPTER 1 MICROWAVE THEORY

1. Introduction of Microwave Technology

As a new technology, microwave treatment of organic contaminated soil is still in the experimental stage. The application of steam distillation is mode one of applying microwave technology to the treatment of hazardous wastes. This study is one stage of a sequence of operations associated with the development of a technology: Stage 1. Benchscale studies to show that the goal can be technically achieved. Stage 2. Preliminary economic calculations to show that the technology is feasible. Stage 3. Pilot Plant studis, a limited scale up of the process to determine if unforeseen problems arise on scale up and the obtaining of better economic data for calculations. Stage 4. Scale up testing the process under field conditions.

This study reported herein is on benchsale studis. The next scale will be the pilot plant studies on the scale of a 50-cubic-foot microwave cavity and a 12-foot conveyor belt. Depending on the soil and waste characteristics, pilot plant will operate 1-5 tons of soil per hour. The contaminated soil will be processed continuously as it moves on the conveyor belt through microwave cavity. The power energy of pilot plant is 6.4 KW (see Figure 1-1: A Sketch of the Proposed Pilot Plant).

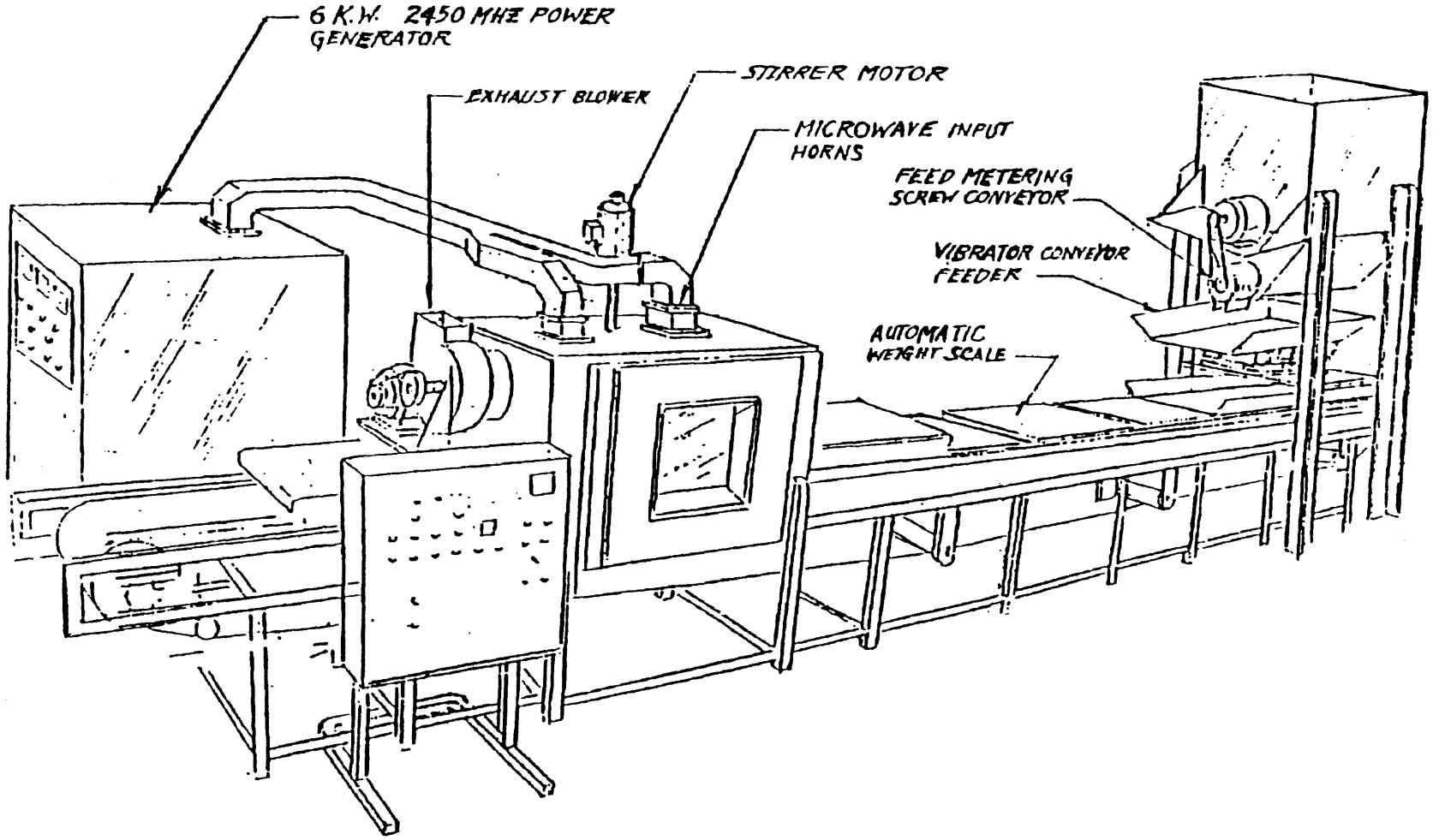


Figure 1-1: A Sketch of the Proposed Pilot Plant

(L. Dauerman & G. Windgasse: The Capital and Operating Costs: Microwave and Incineration, 1989)

Although it is still in the experimental stage, microwave treatment has been found a good hazardous waste treatment process in three aspects:

a. Wide applications. Microwave can treat the most hazardous wastes including organic substances and metallurgical materials.
b. Cost-effective. From the preliminary calculation, the capital and operating costs are low compared with some other technologies.
c. Easy to operate. Microwave decontamination is accomplished in a single stage; the conveyor belt can continuously send contaminated soil into the microwave cavity; also, it is a low temperature and low residence time process.

2. The Theory of Microwave Energy

Microwaves are electromagnetic waves which lie in the frequency spectrum between radio waves and infrared radiation, i.e., approximately 300 MHz to 300 GHz. Thus, the wavelengths involved range from about 1 meter to 1 mm (L. Maley: Microwave Measurement and Control, 1973) (See Figure 1-2: The Electromagnetic Spectrum). All the waves are moving at a speed of 3×10^{10} cm/sec or 186,000 miles/sec.

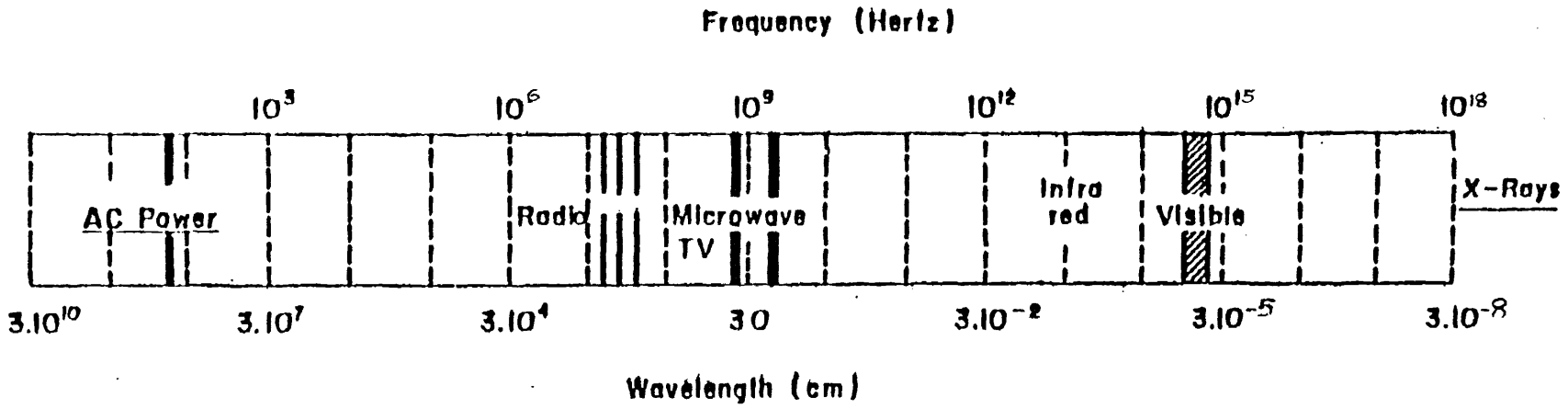


Figure 1-2: The Electromagnetic Spectrum
(L. Maley: Microwave Measurement and Control, 1973)

The movement of wave is in the X-direction. The wavelength is simply the distance between the peaks of the wave. Since the wave is moving at speed of 3×10^{10} /sec (c), therefore, the frequency of wave (f) should be equal to the speed divided by the numbers of the positive or negative peaks (λ). The simply calculation is

$$f = \frac{c}{\lambda}$$

It is clear that different materials with different charges will experience different results when interacting with electromagretic radiation at different frequency. So that different chemicals and atomic constituents have a variety of natural frequencies and also, the effects of its interaction with electromagnetic fields will vary greatly with frequency.

Absorption of microwaves by any material is dependent on several factors. First, consider the absorbtion of the electrical component of the electromagnetic radiation. Conductors absorb only skin-deep. Therefore, depending upon the surface to volume ratio of the conductor, the conductor will act as wither a reflector or a conductor. The non-conductors will act as absorers provided their loss tangents enable the molecules to rotate with frequency of the field. Second, the magnetic component will be absorbed by materials with magnetic domains provided that such materials do not act as reflectors.

The depth of penetration of microwave in the material is dependent on its dielectric properties. In general, the energy transmitted into the substance is progressively

absorbed or attenuated so that the wave decreases in magnitude as it penetrates into the material. Usually, the depth of penetration decreases with the increasing of dielectric properties because most energy are absorbed during the transmitting. On the other hand, insulators and conductors reflect or transmit microwave with very little absorption so that the depth of penetration can reach the maximum in the materials. Two basic parameters will describe the dielectric properties for a certain materials at a given frequency. One is the dielectric constant "e", and the other is loss tangent tan "δ". The wavelengths at 2450 MHz are dependent on the e and the free-space value λ_o, i.e.

$$\lambda = \frac{\lambda_0}{\sqrt{e}}$$

When e is large, the wavelength become small in a material.

The loss tangent tan δ represents the half-power penetration depth D. When tan δ is less than 1, the formula will be:

$$D = \frac{0.269\ \lambda_0}{\sqrt{e} \times \tan \delta}$$

From the two formulas above, it can be concluded that the larger dielectric constant as well as the loss tan the smaller penetration depth.

The values of the dielectric constant and loss tangent are the amount of energy reflected, transmitted and

absorbed by the material.

Usually the dielectric materials have the ability to be polarized by an applied electric field, for example, water, which is a dipolar molecule, has a very high dielectric constant which is about 80 (see Figure 1-3: The Dielectric Constant of Materials). Naphthalene, TCE and other most organic chemicals, on the other hand, are non-polar molecules which cannot be polarized by an applied electric field and have low dielectric constants in the range of 2-3. The interaction of microwave with non-polar organic materials dependens upon the collision with the absorbring dipolar molecules in this material. This causes the temperature of the materialto increases and can thus lead to the volatilization of the non-polar organic present.

The dipolar molecules rotation happens when the particular particle experiences thousands of collisions each time the microwave is cycled. Heat is provided by a two-step energy conversion process. The first step is that the electric field energy is converted into ordered kinetic energy, and the second step is that the electric energy converted into disordered kinetic energy. At this point it is appropriate to regard it as heat. It is important to notice that because of the nonspherical shape, the molecules are not completely free to rotate, and also when

Material	Type	e
Electrolytes	H_2O (3 GHz, 25°C)	77.5
	H_2O (10 GHz, 25°C)	55.0
	NaCl (0.1M, 3 GHz)	76.0
	NaCl (0.7M, 10 GHz)	50.0
Foods, etc.	Clay, 20% H_2O	11.3-20
	Douglas fir	1.8-1.86
	Paper, royal gray	2.62-2.75
	Steak, bottom round	30-50
	Suet	2.5
	Soap, Ivory	2.96
Inorganic Solids	NaCl	5.90-5.98
	Al_2O_3	8.60-10.55
	SiO_2	3.78
	H_2O (ice)	3.17-3.3
	Se (crystalline)	10.4-11.0
	S	3.62
	MgO	9.65
	$(Ba,Sr)TiO_3$	200-7,000
Organic Liquids	MeOH	8.9-31
	EtOH	1.7-22.3
	Glycol	7-39
	CCl_4	2.17
	Neptane	1.97
	Styrene	2.38-2.58
	Nitrobenzene	31.1
Polymers	Acrylics	2.36-2.75
	Alkyds	4.52-4.75
	Amides	3.53-3.03
	Cellulosics	2.80-4.00
	Epoxies	3.01-4.14
	Phenolics	3.08-5.81
	Polyesters	2.72-3.98
	Silicones	3.51-4.02
	Vinyls	
	Kel F	2.26-2.35
	PVC	2.60-2.84
	TFE	2.04-2.10
	Miscellaneous	
	Polystyrene	2.54
	Polyethylene	2.26

Figure 1-3: Dielectric Constant of Materials

temperature is above the zero, because of the already existing thermal agitation, there is a tendency to ranomize the orientation of the molecules.

The amount of water moisture in a substance greatly affects the dielectric constant of the material because of its dipolar properties and high dielectric constant. The water molecule dielectric bonding nature is between its oxygen and two hydrogen atoms. When subjected to an electromagnetic field, its polar properties force it to rotate or vibrate according to the amplitude, direction, and frequency of the electric vector. Therefore, as a larger percentage of water is added to the material, the dielectric constant in the material increases. Thus, this material, such as sand, soil and non-polar organic molecules, can be heated much more easily. A material, such as glass, with very low moisture constant, is almost transparent to microwaves, and thus cannot be heated by microwaves easily.

But, at the same time, because of the large dielectric constant and loss tangent, water is an absorber, therefore, there is less transmission of microwaves. Even a few percent water present in a material may reduce the power level of transmitted microwaves by several times. Conversely, naphthalene, TCE and other non-polar materials have limited effects on the depth of penetration of microwaves in the materials since they absorb a negligible amount of microwave power.

CHAPTER 2 STEAM DISTILLATION

Steam distillations are employed generally for water insoluble compounds having a vapor pressure of at least 5 mm near 100^{o}C. Compounds that are unstable at their boiling points and unreactive with steam can be purified by this process (Charles MacKENZIE: Experimental Organic Chemistry, 1971).

When two immiscible substances such as TCE or naphthalene with water are heated together, each will exert its own vapor pressure independently of the other, and when the sum of the two vapor pressure equals the external pressure, the mixture will boil. Unlike an ideal solution of two liquids, a heterogeneous mixture of immiscible liquids does not follow Raoult's law (John Landgrebe: Theory and Practice in the Organic Labotory, 1977). Instead of each liquid producing a partial vapor pressure that is dependent upon the mole fraction of that liquid present, each liquid of mixture exhibits a vapor pressure which depends only on the temperature. As the temperature is raised, the vapor pressure above the surface of the liquid will increase. When the combined vapor pressure of two liquids equals atmospheric pressure, distillation will commence.

According to the Dalton's Law, the partial pressure P, at a given temperature of each component of the mixture of the immiscible, is equal to the vapor pressure P^{o}, of the

pure compound at the same temperature:

$$P = P^{O}$$

and does not depend on the mole fraction of the compound in the mixture since each component of the mixture vaporizes independently of each other. In contrast, for the solution of miscible liquid, the partial pressure of each constituent will depend on its mole fraction in solution (Raoult's law). The total pressure P_T of a immiscible solution of gases, according to the Dalton's Law, is equal to the sum of the partial pressures of the constituent gases so that the total vapor pressure of a mixture of immiscible, volatile compounds is given by equation of following:

$$P_T = P^{O}a + P^{O}b + P^{O}c \ .....$$

The total vapor pressure of the mixture at any temperature is always greater than the vapor pressure of even the most volatile component at that temperature, due to the contribution of the vapor pressures of the other constituents of the mixture. The boiling point of a mixture of immiscible compounds must then be lower than that of the lowest boiling component (R. Roberts & J. Gilbert & L. Rodewald & A. Wingrove: An Introduction to Modern Experimental Organic Chemistry, 1969).

The organic chemical - naphthalene has boiling point of 218.87^{O}C. The naphthalene study show that when the immiscible solution of naphthalene and water is heated together, the boiling point of the mixture become lower than that the lowest boiling point component which is water. At

$86^{o}C$, because the P^{o} of naphthalene is equal to 10 mmHg, and the P^{o} of water is 750 mmHg, therefore, the solution of naphthalene and water mixture boils at $86^{o}C$ when the atmospheric pressure is equal to 760 mmHg.

As predicted from theory, the boiling point of the immiscible mixture is below $100^{o}C$ which is the boiling point of the water. The low temperature steam distillation is of great use since some chemicals will decompose at higher temperature. This advantage offers a possibility for purification of substances from either steam or non-volatile residues by using condensate system.

CHAPTER 3 A COMPARISON OF MICROWAVE TO OTHER TECHNOLOGIES

a. Other Technologies

1. Radio Frequency

Radio Frequency (RF) technology is to be used for the processing of decontamination of uncontrolled land fills and hazardous substances from spill. Like microwave, radio waves are electromagnetic radiation. The frequencies can be as low as 45 Heretz or extend well above 10 gigaHertz. The choice of operating frequency is dependent on the soil properties.

The development of RF technology started in the middle of 1970s for the recovery of hydrocarbons by heating large volumes of earth in situ. The in situ heating process has been demonstrated to heat large volumes of soils and earth formations rapidly. The concept of in situ decontamination has three requirements: a high temperature (300-400^{o}C) coupled with long residence times (1-2 weeks); the presence of decontamination mechanisms e.g., thermal decomposition, distillation, vaporization, fixation to soil constituents for the destruction or mobilization of the contaminants; and the presence of a gas and vapor recovery mechanism allowing

their collection at the surface (Harsh Dev, ect.: Decontamination of Hazardous Waste Substances from Spills and Uncontrolled Waste Sites by Radio Frequency In Situ Heating, 1984)

The radio frequency equipment can be placed above the landfills. The composition of equipment mainly includes a vapor barrier, collection lines for carrying the gases into the vapor barrier, coaxial cables for carrying the RF power into energize electrodes, liquid/ gas separator, condenser and a induced draft fan (see Figure 3-1, Preliminary process flow diagram for decontamination of landfills by radio frequency). Both liquid and gases can be incinerated on site.

The developers of the process claim that hazardous substances including the Organic substances, such as chlorinated hydrocarbons, and metallic wastes can be treated with radio frequency in situ. They have claimed in that the incineration of hexachlorobenzene (HCB) by RF can reach 99.998 percent decomposed at 1000^{o}C with residence time of 2 seconds.

The methods of heating process include the thermal decomposition which is using the high temperature incineration (the temperature is usually ranged from 400-1000^{o}C) to decompose organic chemicals; the distillation which is according to the presence of moisture in landfills, to heat hydrocarbons (HC) contaminated soils to 300-400^{o}C, and cause HC to be vaporized. This process would recover a large fraction of the compounds.

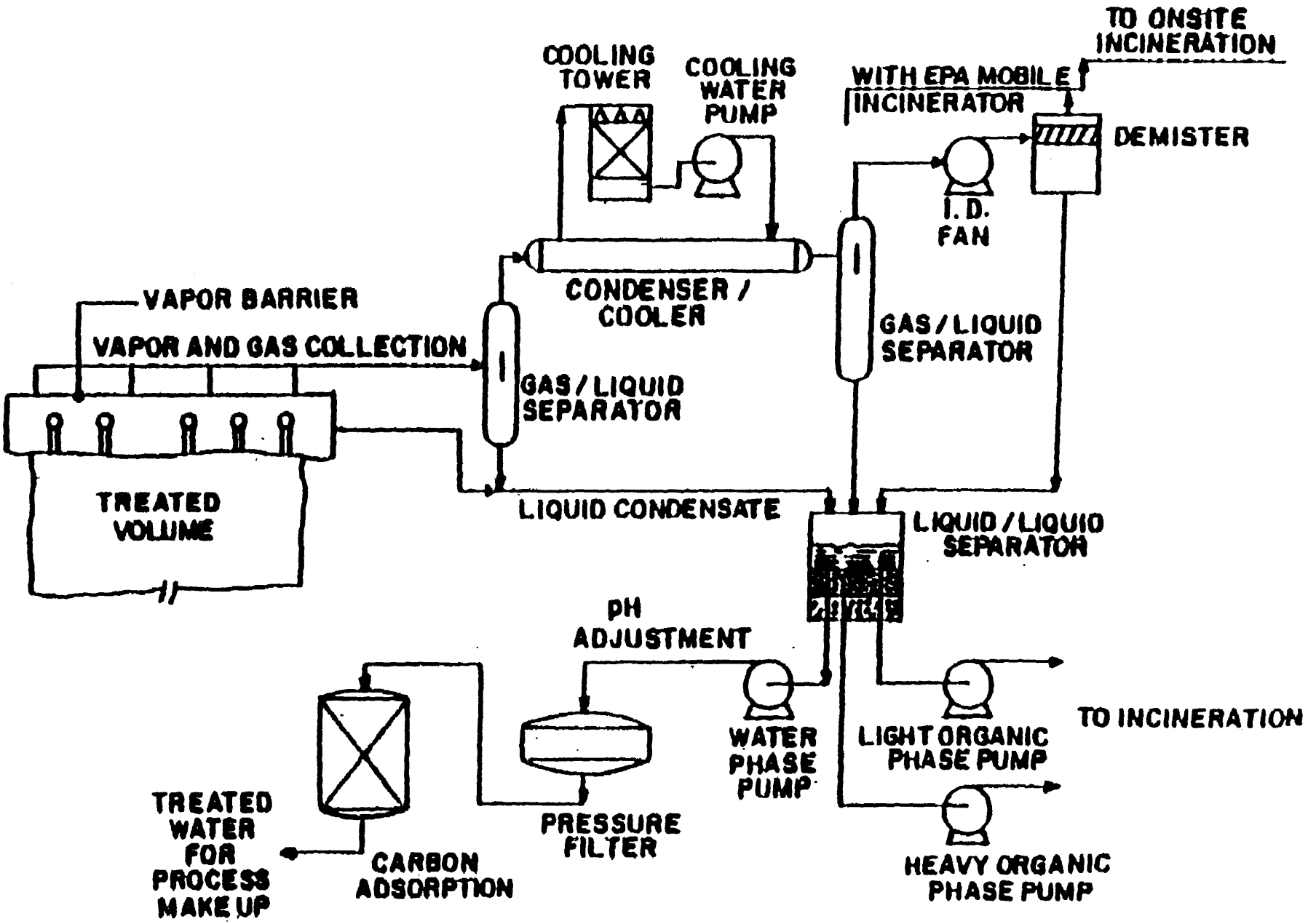


Figure 3-1: Preliminary Process Flow Diagram for Decontamination of Landfills by Radio Frequency (H. Dev, etc.: Decontamination of Hazardous Waste Substances from Spill and Uncontrolled Waste Site by Radio Frequency in Situ Heating, 1984)

While there are similarities between RF heating and microwave heating, there are also significant differences. RF was developed to heat up shale stone. These materials have very low relaxation times. Therefore, it is necessary to use a low frequency of radiation. Also, at low frequencies, absorption of energy is decreased. In contrast, microwaves operate at higher frequencies can be achieved in shorter times. Another difference is that RF reception antennas have to be placed in the site to receive the transmitted RF energy. On the other hand, microwave energy can be transmitted to the contaminated soil by placeing "leaky" waveguides over the surface.

2. Rotary-Kiln Incineration

Rotary-Kiln incinerators are specially used for disposing of coal tar, as well as solid organic chemicals, such as naphthalene. Such incinerator is a controlled high-temperature oxidation process that converts the principal elements (carbon, hydrogen, and oxygen) in most organic compounds to CO_2 and H_2O. Based on destruction of the molecules, rotary-kiln consequently eliminates the toxic or hazardous property of the tar and organics. The existence of elements other than carbon, hydrogen and oxygen in a waste may, on incineration, results in the production of gaseous or particulate pollutants that require removal in off-gas treatment systems (see Figure 3-2, Rotary Kiln Incinerator).

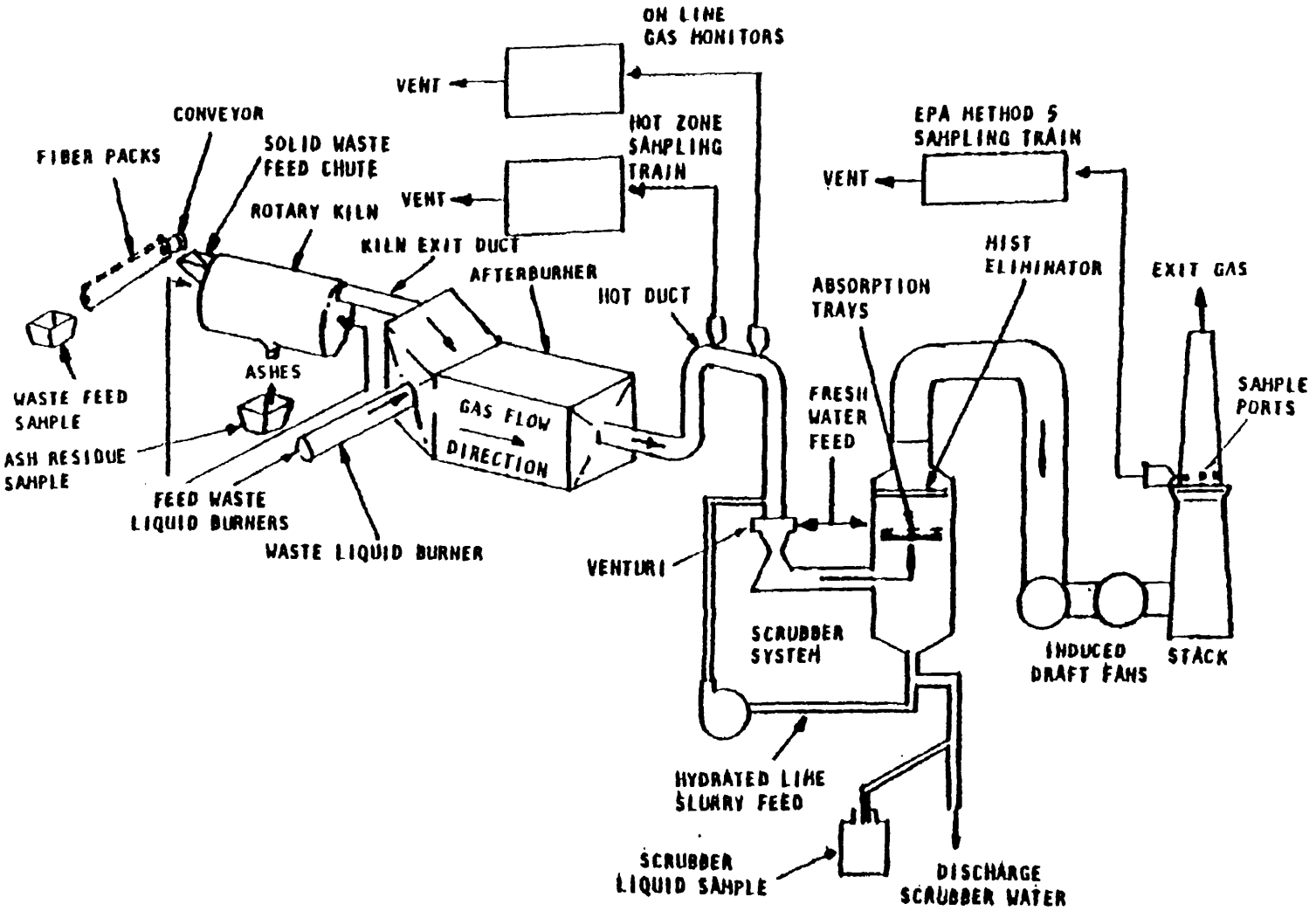


Figure 3-2: Rotary Kiln Incinerator
(E. Martin, etc.: Hazardous Waste Management Engineering, 1987)

The rotary- kiln is a cylindrical shell lined with refractory material that is horizontally mounted at a slight incline. The kiln typically has length-to-diameter ratios between 2:1 and 10:1 and is normally rotated at speeds between 1 and 5 rpm. Combustion temperatures are between 850^{o}C and 1650^{o}C, and residence times vary from several seconds to hours, depending on the type of waste being processed. The rotating kiln causes a tumbling action that effectively mixes combustible solids with air to promote complete burning of the waste. Noncombustible waste travels down the inclined kiln and is collected in drums after water quench cooling (Gaynor Dawson & Basil Mercer: Hazardous Waste Management, 1986). As required by RCRA, the destruction of principal organic hazardous constituent (POHC) has to be reached 99.99 percent by incineration and the emission of hydrogen chloride has to be limited.

In rotary kiln incineration, it is not possible to effect steam distillation because heat is transferred from hot air to the soil. This mode of energy transfer establishes a thermal gradient across the soil particles causing the diffusion of the water out of the particles into the hot air stream. This diffusion mechanism renders steam distillation impossible. Therefore, high temperatures are needed to volatilize the organics, higher than even the boiling points of organic contaminants for the following reasons: heat transfer decreases with increasing temperature

because of both the diffusion of water out of the soil particles and, also, because of the formation of an insulating slag surrounding the particles.

The advantages of rotary kiln incinerator are: it is highly developed technology equipped with air pollution control system that emit only minimal amount of pollutants; The 99.99 percent of organic wastes can be destructed efficiently. The major disadvantage of the rotary kiln incinerator is that the the capital and operating costs for incinerator have substantially increased, it dose not appear to be the most economical disposal method (Gaynor Dawson & Basil Mercer: Hazardous Waste Management, 1986).

b. Comparative Merits of Microwave and Incineration

1. General Considerations

1). Steam distillation is effected batchwise in the chemical industry by the direct introduction of steam into the substrate to be treated. In contrast, microwave treatment of contaminated soil is a continuous process because the steam is formed directly by the microwave absorption.

As mentioned before, it is not possible to effect the steam distillation in a rotary kiln because heat has to be transferred from hot air to the soil.

2). With microwave treatment, contaminants are not destroyed but are recovered; with incineration, contaminants are destroyed forming volatile pollutants.

3). Incineration cannot be a politically acceptable remediation technology in some communities. In contrast, microwave will not be subject to similar attacks because it is a low temperature operation.

4). Incineration may cause heavy metals in soil in non-hazardous states to be changed to hazardous states after treatment. For example: lead sulfate which is insoluble and non-leachable is converted into lead oxide after high temperature heating. Lead oxide is soluble and leachable. The irony is that soil after incineration treatment poses a greater remediation problem than before.

5). Incineration, a high temperature process, will cause the evaporation of heavy metals which are volatile (and in the metal state) such as lead and mercury. There will be a need for complex and expensive control technologies. Microwave, operating at low temperatures, will not cause this problem.

6). With incineration, the end product is an ash which has to be landfilled. The end product of microwave treatment is recovered soil.

7). It has been assumed that in microwave heating the soil thermally equilibrates with the added water. The heating of the soil represents the major cost. In fact,

such equilibrium is improbable because microwave radiation directly heats the water which is the greatest absorber, therefore, vaporization occurs as a result of direct heating rather than from thermal equilibrium with the surroundings. Thus the actual heat needed may be significantly less than was calculated.

2. Economic Comparison

The capital and operating costs, respectively, were compared for the treatment of contaminated soil by two different technologies, namely, microwave induced steam distillation and incineration. It was concluded that treatment by microwave was more cost-effective because the capital cost is one tenth that of incineration; the operating cost, one forth the cost of incineration.

The incineration cost is based upon the double rotary kiln sold by American Combustion Inc., Norcross, Georgia which is recommended for soil incineration. The information was obtained from the vendor's brochures and conversations with Fred Kuntz, Incineration Projects Manager.

The microwave costs were based upon negotiations to install a pilot plant with Bernard Krieger of Cober Electronics, Inc. and Frank Smith of Microdry, Inc.; also, the paper titled, "Economic Assessment of Microwave and

Radio-Frequency Materials Processing," by Professor Philip S. Schmidt, Department of Mechanical Engineering, Center for Energy Studies, The University of Texas, Austin, Texas, and Michael R. Sanio, Ontario Hydro, Toronto, Canada presented at the 23rd Microwave Power Symposium Held in Ottawa, Canada on August 29-31, 1988.

The Summary of Comparative Costs:

Microwave and Incineration

Basis: processing rate of 5 tons/hour

	Capital	Operating
Cost/Ton		
Microwave	$ 500,000	$ 40
Incineration	$ 5,500,000	$ 175

The Summary of Microwave Costs:

1). Assumptions

Basis	1 ton of soil
Processing Rate	5 tons per hour
Contaminant Level	1000 ppm
Molecular Weight of Contaminant	1000
Vapor Pressure of Contaminant @100^{o}C	15 mmHg
Inference:	
Ratio of water/contaminant to effect steam distillation	50 : 1

2). Capital Costs

Assumption: the "plug to heating" efficiency is 80%

Power Supplies (@ $ 1000/kw) ----------$ 146,000

Cavity, Waveguides, et al(@ 1.5 x power supplies) ----------$ 234,000

Total ----------$ 380,000

3). Power

Assumption: 5 tons/hour process rate (rate of rotary kiln)

stay time (min/ton) ---------- 12

energy (@23.33 kwh/ton) ---------- 83.9

mega J power ---------- 117 kw

power (@ 80% efficiency) ---------- 146 kw

4). Operation Costs

Basis: 1 ton of contaminated soil; Assumption: "plug to heating " efficiency is 80%, thus energy needed is 29.16 kwh

Power cost ($ 0.05/kwh) ----------$ 1.46

Magnetron replacement ($ 0.06/kwh)--------$ 1.75

Maintenance ($ 0.10/kwh)----------$ 2.92

Labor ($ 1.15/kwh)----------$ 33.53

Total ----------$ 37.66

5). Energy

Basis: 1 ton of contaminated soil

Component	Wt (lb)	Sensible Ht.(kwh)	Latent Ht.
soil	2000	20.16	
contaminant	2	0.0534	0.1055
water	9	0.450	2.565
Total ----------		23.33 kwh/ton	

@ 100% "plug to heating" efficiency

6). Sensible Heat (40 --212^{O}F)

Basis 1 lb

Component	Wt.(lb)	Sp.Ht.	Energy (btu)	Energy(kwh)
soil	1	0.2	34.4	0.01008
water	1	1.0	172	0.0504
contaminant	1	0.45	77.4	0.02267

7). Latent Heat

Basis: 1 lb

Component	Wt. (lb)	Energy (btu)	Energy (kwh)
water	1	973	0.285
contaminant	1	180 *	0.05274

* Representative organic latent heat

(Leonard Dauerman & Gabriele Windgasse: Comparative Capital and Operating Costs of Microwave and Incineration, 1989)

CHAPTER 4 REGULATIONS:

ORGANIC-CONTAMINATED SOIL

The improper management of hazardous waste is probably the most serious environmental problem in the United States. In 1979, EPA estimated that only 10 percent of all hazardous waste was managed in an environmentally sound manner. The remainder was transported, treated, stored or disposed of in a way that potentially threatens human health and the environment.

Because of these problems, to enforce laws governing the management of hazardous waste and to develop effective waste treatment technology without at the same time damaging the environment and human health is of vital importance to the human race.

Naphthalene and trichloroethlene (TCE) are two major toxic pollutants which cause serious soil contamination.

1. Naphthalene-Contaminated Soil

Naphthalene is the most abundant single constituent of coal tar. In 1974, 1.8 x 105 metric tons of naphthalene were produced from coal tar, and 1.1 x 105 metric tons were produced from petroleum (EPA: Ambient Water Quality Criteria For Naphthalene, 1980). The land disposal of the end products of coal tar and petroleum can cause the large amount of soil contaminated by naphthalene if an accident happens.

1). Federal Regulation: The Resource Conservation Recovery Act (RCRA) is an amendment to Solid Waste Disposal Act which was passed in 1976. Naphthalene is a acute toxic substance defined by RCRA.

Designating hazardous wastes by EPA has two approaches: (1) list and (2) criteria thresholds for waste properties.

Hazardous wastes in the Listing are divided to be four categories: K Code wastes which are from the specific sources; F Code wastes which are from non-specific sources; U Code wastes which are toxic wastes and , P Code wastes which are acute hazardous wastes.

Naphthalene is included in the U code wastes of the hazardous substances list of RCRA which are defined as toxic waste. When such wastes are to be stored, transported, and disposed of by treatment, storage, disposal (TSD) facilities, a permit has to be issued by EPA or by an authorized state government agency. The maximum quantity of the storage of the U code waste is 1000 kg/month at the hazardous waste site, and it must be sent to the TSD facility after the maximum quantity is reached.

EPA has identified the wastes' criteria thresholds which are based on comparison of material characteristics. Any solid waste that exhibits one or more of them is classified as hazardous under RCRA. The characteristics are:

Ignitability - with a flash point of 140^{O}F or less.

Corrosivity - with PH less or equal to 2 or above 12.5.

Reactivity - reacts with water form explosive mixture.

EP Toxicity- (see below for definition)

Naphthalene, a solid under room temperature, has high flash point of 174^{O}F, and is not ignitable. In addition, with a PH value of 8, it is not a corrosive chemical. Moreover, as a organic chemical, naphthalene is not exhibiting any reactive characteristic including with water. The term of EP toxicity is a name of a test designed to identify wastes likely to leach hazardous concentrations of particular toxic constituents into the ground water as a result of improper management (RCRA Manual, 1989). Naphthalene is mobile in the soil. In the landfills, it is possible for naphthalene moving to the deeper layers of soil and it has the tendency of contaminating ground water. The solubility of naphthalene in water has been reported to range between 30,000 ug/l and 40,000 ug/l at 25^{O}C (EPA, Ambient Water Quality Criteria for Naphthalene: 1980). From this point, naphthalene is a hazardous waste.

Federal laws have no soil criteria for most toxic chemicals. For nearly all the contaminants, there are no soil threshold limits defining when hazardous effects will

begin to be evidenced (G. Dawson & B. Mercer: 1986). The important criteria for soil contamination is its ultimate ability to contaminate air and water. Thus contamination of air and water is used as the standard and guideline of the hazardous level in soil.

2) State Regulation

Environmental Cleanup Responsibility Act (ECRA) is State Law of New Jersey and became effective on December 31, 1983. This law "imposes pre-conditions on the sale or closure of Industrial Establishments involved in the generation, manufacture, refining, transportation, treatment, storage, handling, or disposal of hazardous substances or hazardous wastes" (New Jersey DEP).

State Laws also define the hazardous wastes through the listing and the criteria of waste characteristics.

The list of hazardous wastes of State New Jersey has five parts which are different from federal laws. The five parts are: (1) Petroleum and Petroleum Products; (2) Prohibited, Restricted and Specially Restricted Pesticides; (3) Substances Designated as Hazardous Substances by the EPA in the Clean Water Act; (4) Substances Designated as Toxic Pollutants in the Clean Water Act; (5) Other Substance. Naphthalene is included in Part 1, 3, and 4 as a hazardous substance. It is not included in any other part of this list.

The waste characteristics designated by New Jersey are the same with the RCRA, except the last one - EP Toxicity. The definition of EP Toxicity given by DEP is " the extract from a representative sample of the waste contains any of the contaminants listed in Table 1, or....., at a concentration equal to or greater than the respective value given in those tables". Naphthalene is not included in Table 1, so that it is not EP Toxicity and, it does not exhibit any of hazardous characteristic.

To contrast with RCRA, ECRA has listed hazardous constituent criteria for soil contamination. In N.J.A.C. 7:26-8.15, Discarded Commercial Chemical Products, Off-Specification Species, Containers, and Spill Residues Thereof mention that: (d) Any residue or contaminated soil, water or other debris resulting from the cleanup of spill, into or on any land or water, of any commercial chemical product or manufacturing chemical intermediate having the generic named listed in subsections 8.15 (e)..... Naphthalene is a hazardous substance on the list and with the State Hazardous Waste Number of U 165. Therefore, by definition of New Jersey laws, Naphthalene contaminated soil is hazardous waste.

2. Trichloroethylene-Contaminated Soil

Trichloroethylene (TCE), as an equipment cleaner and degreaser, is widely used by industries. The waste stream of TCE from the open dumping or improperly operated land disposal heavily contaminated the soil. TCE contaminated soil involved in the pollution of ground water--the source of drinking water is more dangerous than soil contamination itself. In many of these cases, ground water supplies are badly contaminated with such toxic or cancer-causing chemicals.

1). Federal Regulation

In the Hazardous Waste List of RCRA, TCE is in the F Code which is defined as a waste from non-specific sources. F Code wastes have characteristic of solvent. Most of F Code solvents are not allowed to be disposed or landfilled without treatment with distillation or incineration since they are liquid and, some of them are flammable.

TCE has no hazardous waste characteristic of ignitability because it is nonflammable (Micheline Kirsch-Volder: Mutagenicity Carcinegenicity, and Teratogenicity of Industrial Pollutants, 1982). It is not corrosive and reactive with water either. From the definition of EP Toxicity of RCRA, since TCE has fast mobility in the soil, it most likely has a tendency to contaminate ground water. Therefore, TCE is hazardous waste by EPA criteria.

2) State Regulation

As mentioned before, the Hazardous Waste list in ECRA of New Jersey is constituted by 5 major parts. As the same with Naphthalene, TCE is included in 3 parts of this list. Because the definition of petroleum and petroleum products given by DEP in Part 1 is that "all hydrocarbons, and mixture of hydrocarbons, which are liquid at one atmosphere pressure and temperatures between -20^{0}F and 120^{0}F, and all hydrocarbons which are discarded in a liquid state at or nearly at atmosphere pressure at temperature in excess 120^{0}F.....", thus TCE is included in this part of Hazardous Waste List. TCE also can be found in the Part 3, "Substances Designated As Hazardous Substances by the U.S. EPA Pursuant Section 311 (b) (2) (A) Of the Clean Water Act" as well as Part 4 "Substance Designated as Pollutants under Section 307 (a) (1) of the Clean Water Act.

TCE contaminated soil is under the ECRA regulation too. In Section of N.J.A.C. 7:26-8.15: Discarded Commercial Chemical Products, Off-Specification Species, Containers, and Spill Residues Thereof, TCE is in table 1 which is the chemical as a hazardous substance in constituent of either contaminated soil or water.

It can be concluded that both wastes of Naphthalene and TCE, both Naphthalene and TCE contaminated soil are hazardous wastes from both federal and State regulations.

CHAPTER 5 EXPERIMENTAL

A. Methods

1. Gas Chromatograph

The GOW-MAC series 580 Flame Ionization Gas Chromatograph has been used for naphthalene and TCE studies. It is single detector and single column unit for isothermal operation.

When sample is injected onto the head of the column, it becomes vaporized and the elution is brought about by the flow of an inert gaseous mobile phase.

a. Carrier Gas Supply

The helium is chosen to be a carrier gas in this GC since the carrier gas must be chemically inert and dictated by the type of detector used. the flow rate of Helium is controlled by the pressure regulator. The inlet pressure in the operation is set at 40 psi; the flow rate is set at 30 ml/min. The TCE study showed that if the flow rate of helium

is changed from 30 ml/min to 50 ml/min, TCE peak become broad and smaller, peak area decreased about 21% since increase the carrier gas flow rate increase the elusion rate and decrease the sample rotation time.

b. FID Detector

The Flame Ionization Detector is a widely used detector. It is designed for high sensitivity performance and low noise. The Hydrogen and Air are the sources of the flame. The mixing ratio of H_2/air determine the temperature of the flame. Organic compounds are to be pyrolyzed at certain temperature. The mixing ratio of H_2/air also determine the sensitivity of the detector. Increasing the air flow rate (decreasing the ratio), for example, results in the low sensitivity of the detector in the TCE study.

The electrical amplifier of detector increases the signal but also the background noise. The range which can be chosen is from 10^{-9} to 10^{-12}. A good separated peaks appeared in TCE and naphthalene studies are at the range of 10^{-11}.

The attenuation is used to scale the peak heights which range from 1 to 1024. Because detector has different sensitivities to different compounds, therefore, the the good separated TCE peak appears when the attenuation is set at 16, and for naphthalene is 32.

c. Column

The column used in this GC is 4' x 1/g" stainless steel packed with 5% ov-101 on chromasorb P, AWDMCS, 80/100 mesh.

The column efficiency requires that sample of suitable size and be introduced as a "plug" of vapor (Douglas Skoog: Priciples of Instrumental Analysis, 1985); In both TCE and naphthalene studies, microsyringes are used for injecting 4 ul samples to the column.

The column temperature is dependent on the boiling point of the sample compound since the sample is required to be vaporized at the head of column. Theoretically, the temperature of the column should be equal to or sightly above the average of the compound boiling point. Naphthalene is a non-volatile organic compound, has boiling point of 218.17^{o}C, but the column temperature was set to 150 during the the naphthalene study, and also, TCE has boiling point 87^{o}C, the column temperature was set 50^{o}C during the TCE study.

With regard to the sample evaporation, the injection temperature is also important for controlling column efficiency. Usually, the injection temperature is ordinarily about 50^{o}C above the sample boiling points.

2. Gas Chromatography/Mass Sectrometry

The model of GC/MS equipment used in this study is HP 5890A-GC and HP 5970B-MSD.

The advantage of GC/MS rather than GC alone is that the flow rate of sample from capillary columns is generally low enough that the column out put can be fed directly into the ionization chamber of the mass spectrometer. Because of this reason, the direct coupling of these columns to the ion source is feasible, thus enhancing sensitivity (Douglas Skoog: Priciples of Instrumental Analysis, 1985).

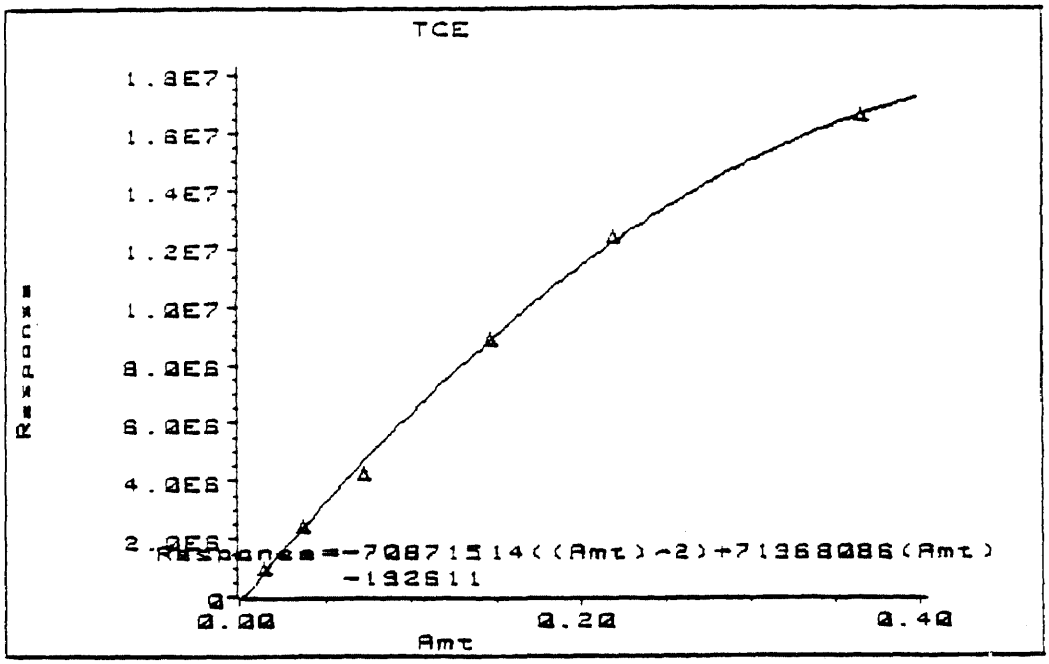
For TCE study, the mass number in GC/MS is set from 130 to 135 because TCE molecular weight is 131; 20 min and 50 sec. is chosen for TCE running time because TCE peak appears around 10 minutes. The temperature program is also selected for TCE study. The initial column temperature is $40^{O}C$, and the end temperature is $180^{O}C$. According to the standard concentration of TCE, the calibration curve is made, and TCE sample are run at the condition as same as the standards (see Figure 5-1).

*** Calibration Table ***

TCE IN METHANOL 10-250ppm

Last Update: 10 Jan 89 11:40 am
Reference Peak Window: 5.00 % of Retention Time
Non-Reference Peak Window: 5.00 % of Retention Time
Sample Amount: 0.000 Uncalibrated Peak RF: 0.000 Multiplier: 1.000

Ret Time	Pk#	Signal Descr	Amt ng/ul	Lvl	Areal	Pk-Type	Partial Name
10.295	1	130.00- 135.00 amu	0.01464	2	1011941	+	1 TCE
			0.03661	3	2457797		
			0.07321	1	4253081		
			0.1464	4	8847238		
			0.2196	5	12398595		
			0.3660	6	16593068		



EXTENDED PEAK INFO Rev 3.1.1 31-Mar-86

Calibration Table : DATA:SFKC-CAL.Q

Ret Time	Pk#	Signal Descr	Amt ng/ul	Lvl	RespFact	Pk-Type	Partial	Name
10.295	1	130.00- 135.00 amu	0.01464	2	14.47e-9	+	1	TCE

Compound name : TCE

Curve Fit : 2nd order, Ignore Origin

Quantitate Referenced to:
ISTD 1 Internal Standard Not Currently Defined

Confirm Presence of Compound Based Upon:
Signal Descr Expected Resp Limits

Figure 5-1: GC/MS Conditions for TCE

3. Extraction

Extraction is a method of separating organic compounds from the mixtures. The distribution of a solute can be between two phases: liquid-liquid or solid-liquid. The Distribution Coefficient, K, can be expressed as following:

$$K = \frac{\text{concentration of A in s.}}{\text{concentration of A in s'}}$$

Here, A indicates the compound, the s and s' are the two phases in which A distribution happens.

1). Soxhlet Extraction

Soxhlet extraction is convenient for separation of a compound in a solid-liquid phases. In naphthalene and TCE studies, soxhlet extraction is used for separation of naphthalene and TCE compounds from soil by using methanol solution. The soil in this study represents the solid phase and methanol is the liquid phase.

This extraction method can be a continuous process. During the operation, soil sample is placed in a porous thimble, extracting methanol solvent is in the boiling flask which is heated to reflux, and distillate as drops from the condenser, then, the solution is collected in the chamber. By coming in contacting with the solid in thimble, the

liquid effects the extraction (Royston Robers, etc.: An Introduction to Modern Experimental Organic Chemistry, 1969). After chamber fills to the level of the up in the arm, the solution empties from this chamber into the boiling flask. In naphthalene and TCE studies, this process usually continues for 24 hours (see Figure 5-2, The equipment Soxhlet Extraction).

2). Ultrasonic

Ultrasonic is usually used for cleaning or digressing, it is also good for solid-liquid phases extraction.

Ultrasonic extraction is based on a process called "cavition" and a subsequent process called "implosion." During "cavition," ultransonic wave transducer causes bubbles or tiny vacuum cavities to form in the liquid. During "implosion," these bubbles collapse, and release large amounts of energy, whose "scrubbing" effect can do wonder. In naphthalene and TCE studies, the soil sample with methanol solution is placed in the bottle in the ultrasonic tank, the energy from sound causes the bottle shaking.

After shaking for a few minutes, the organic compounds are separated from the soil into the methanol. The longer the time used for shaking, the higher efficiency of the separation, since both naphthalene and TCE have higher affinity to methanol than soil.

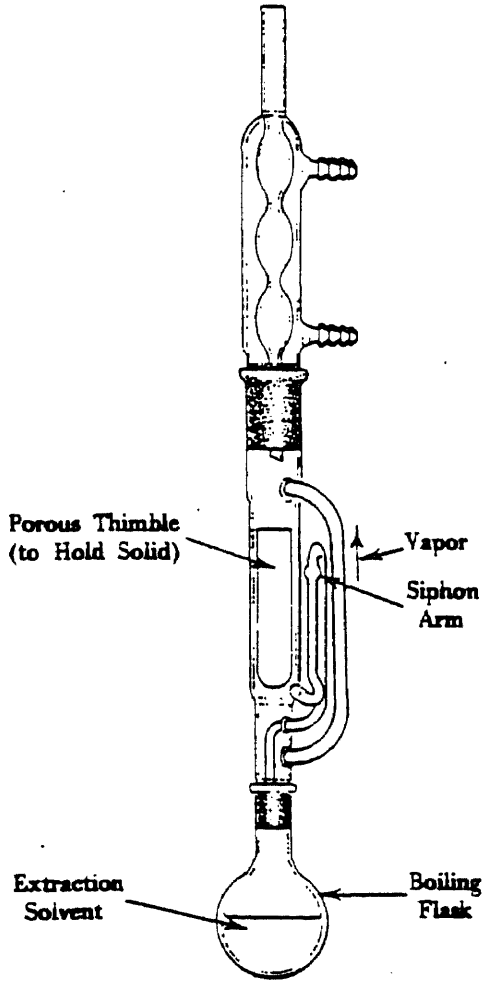


Figure 5-2: Soxhlet Extractor
(R. Roberts, etc.: An Introduction to Modern Experimental Organic Chemistry, 1969)

The NEY Ultrasonik model 300 series is used for the ultrasonic shaking experiment. The power of this equipment is set to the maximum and the degas is set to the minimum, so that the frequency of the shaking reaches the maximum.

4. Microwave Oven

The microwave oven used for this study is SHARP Carousel II Convective Microwave (household model) made by SHARP Electronics Corporation:

Serial NO. 19763

Model No. R-8560

Manufactured 7/85

This oven operates at 2450 MHZ. In a magnetron oscillating electrons within a magnetic filed produce electromagnetic radiation, which is transmitted through a waveguide into the cavity of the oven (See Figure 5-3, The Basic Microwave System in a Microwave Oven) (Gabriele Windgasse: New Hazardous Waste Treatment Technology Utilizing Low Power Dencity Microwave Energy, 1988).

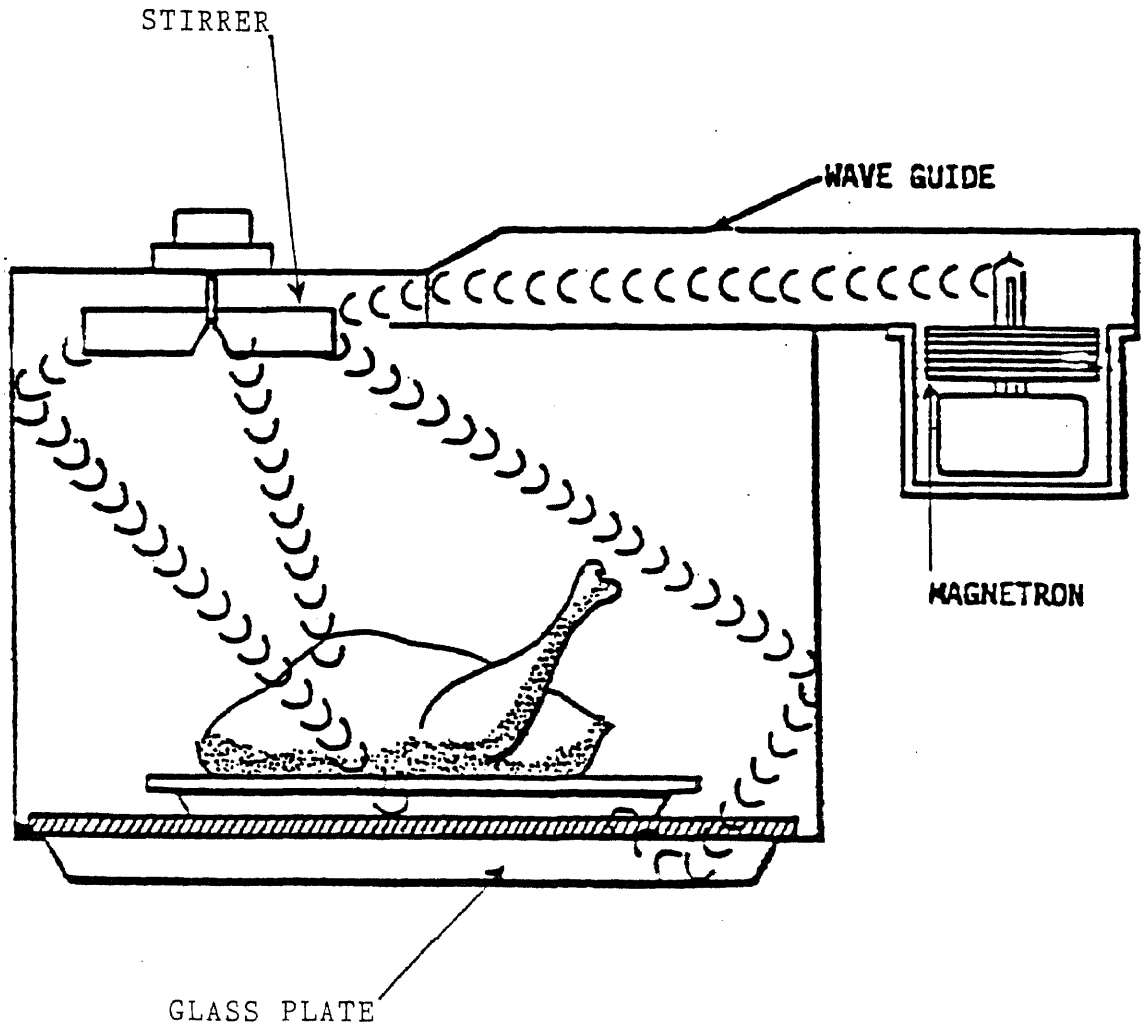


Figure 5-3: The Basic Microwave System in a Microwave Oven
(G. Windgasse: New Hazardous Waste Treatment Technology Utilizing Low Power Density Microwave Energy)

B. Properties of Materials

1. Soil Characteristics

Based on the geological consideration, New Jersey Brunswick soil is chosen for Naphthalene and TCE studies.

The major formation of Brunswick soil is hematite-stained red shales with some interbedded sandstone. The central part of the soil is filled with the mudstone and siltstone (see Figure 5-4, Brunswick Soil Structure).

The soil sample was collected from a filed in south BoundBrook, New Jersey. Soil engineering test was conducted by the Department of Environmental Engineering, New Jersey Institute of Technology. The results showed that the soil sample contain an average liquid limit of 26%, a plastic limit of 11.5%: the natural moisture constant is 19.1%; clay minerals comprised 18% of the Brunswick sample (Thomas Pisciotta: Saturated Hydraulic Conductivity of Brunswick Soil with Aqueon Benzen Solution, 1985).

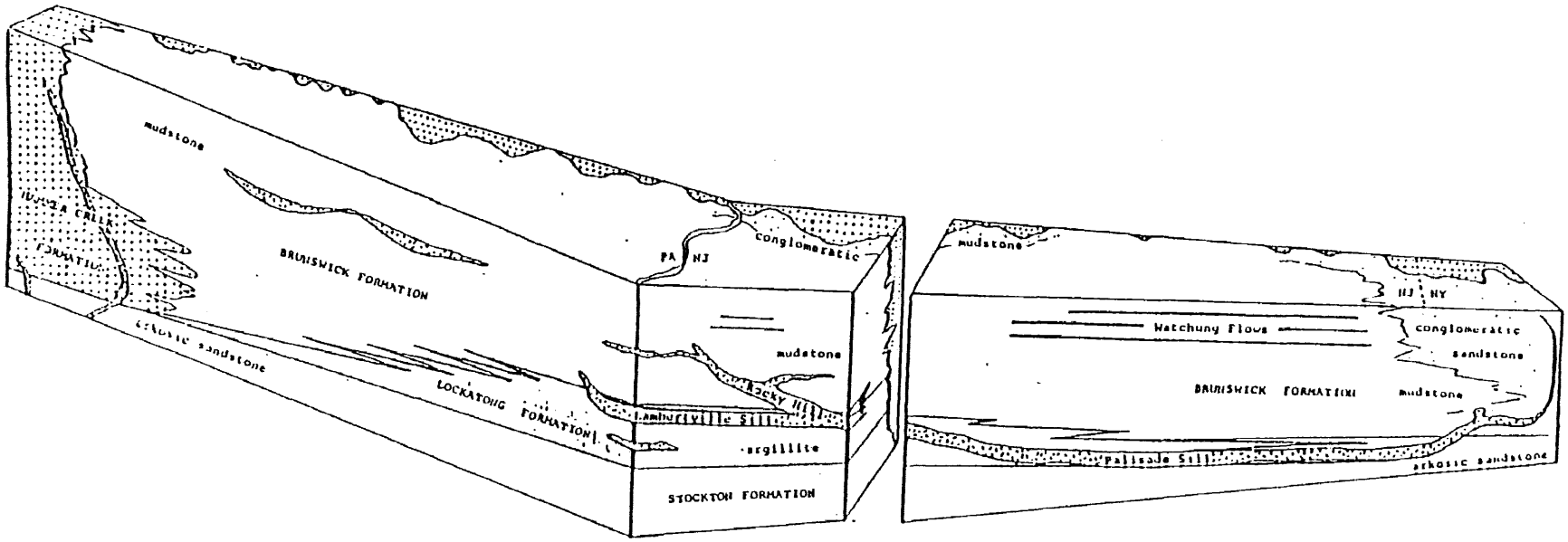


Figure 5-4: Brunswick Soil Structure
(T. Pisciotta: Saturated Hydraulic Conductivity of Brunswick Soil With Aqueon Benzen Solution, 1985)

2. Naphthalene (Chemical, Physical, and Toxicological Properties)

Naphthalene ($C_{10}H_8$) is a colorless solid, non-volatile in a room temperature. The molecular weight of naphthalene is 128.17, boiling point 218.87°C, a vapor pressure of 0.2 mmHg at 20°C.

Naphthalene is on the Workplace Hazardous Substance List and regulated by OSHA. It is also cited by AGGIH, DOT and the State Department of Environmental Protection. In RCRA Hazardous Waste List, naphthalene is in the U code section, which is a toxic Waste section. The legal airborne permissible exposure limit (PEL) is 10 ppm averaged over an 8-hour work-shift.

Naphthalene has toxic effect on the human liver, blood and kidneys.

3. Trichloroethylene (Chemical, Physical, and Toxicological Properties)

Trichloroethylene (TCE) (C_2HCL_3) is a widely used chemical in industrial cleaning and digressing. It is colorless, volatile liquid with a characteristic odor. The

Molecular weight of TCE is 131, boiling point 87°C, vapor pressure 77 mmHg at 25°C.

TCE is also in the Workplace Hazardous Substance List. It is regulated by OSHA and cited by ACGIH and NIOSH. It is regulated by RCRA and the State of New Jersey also. The recommended airborne exposure limit is 25 ppm averaged over a 10-hour workshift.

Because of its widespread dumpling and high toxicity, TCE contamination is a serious problem in the environment. The toxic effect of TCE is mainly on the human liver and central never system.

Comparison of Naphthalene and TCE Characteristics

	Naphthalene	TCE
Mol. W	128.17	131
Boiling P	218.87°C	87°C
Vap.Pre.	0.2 mmHg	77 mmHg

CHAPTER 6 Napthalene Study

A. APPROACH OF THIS STUDY

The purpose of this study is to determine the microwave decontamination of relatively non-volatile materials from substrates such as soil in a batchwise operation. The underlying unit operation is steam distillation which is effected by microwave radiation to cause volatilization of the chemical from soil. This technology must also be studied on pilot plant scale to determine the feasibility of utilizing the process on an industrial scale. The studies were caused out on a benchscale. The results will be used to define the operating parameters in the pilot plant scale of generation.

In the pilot plant scale, an important operational parameter is the depth of the soil layer to be placed on the conveyor. That depth should be the maximum which the microwave energy can penetrate to assure decontamination of all the soil. The goal of this study is to obtain an approximate value for that depth of penetration.

B. EXPERIMENTAL

1. Preparation of Standards

1). Naphthalene Solution Preparation:

Methanol is used as a solvent for naphthalene. Methanol and naphthalene peaks are found to be very well separated in GC analysis.

The preparation of 1000 ppm naphthalene solution standard is as the follows:

0.5 g naphthalene was taken and diluted by 500 ml methanol solution, the calculation is :

$$\frac{0.5 \text{ g naphthalene}}{0.9625 \text{g/ml density}} = 0.51948 \text{ ml naphthalene}$$

$$\frac{0.51948 \text{ ml}}{500 \text{ ml}} = \frac{x}{10E6}$$

$x = 1039 \text{ ppm} \sim\sim 1000 \text{ ppm}$

Naphthalene standard concentrations of 150 ppm, 100 ppm, and 50 ppm were derived from this standard by dilution.

2). The calculation of 500 ppm naphthalene contamination of 30g soil from 1000 ppm naphthalene solution:

$$\frac{x \text{ g naphthalene}}{30 \text{ g soil}} = \frac{500 \text{ g naphthalene}}{10E6 \text{ g soil}}$$

$$x = 0.015 \text{ g} = 15 \text{ mg}$$

If 15 mg naphthalene is needed for 500 ppm naphthalene in 30 g soil, it is necessary to take 15 ml napthalene solution from the 1000 ppm naphthalene solution; 1 ml of 1000 ppm naphthalene solution contains 1 mg naphthalene and 15 ml naphthalene solution contains 15 mg naphthalene.

3). GC (series 580 FID, GOW-MAC instrument Co.)

Standard Conditions for Naphthalene Analysis

The conditions are chosen for naphthalene are as follows:

Temperature:

Injection: 200°C

Column : 150°C

Detector : 200°C

Flow rate :

Helium : 30 ml/min

H_2 : 20 ml/min

Air : 120 ml/min

Attenuation and range : 32 x 10E-11

Average of Standard Peak Areas:

Concentration of Naphthalene ppm	Peak areas
50	5.12 x 10E-10
100	9.2 x 10E-10
150	1.23 x 10E-9
250	2.04 x 10E-9

(See also Figure 6-1: Average of Standard Areas)

a = 0.5911
b.= 12.68033505

2. Microwave Treatment

1). Blank

30 g soil is mixed with 15 ml 1000 ppm naphthalene, the mixture is then extracted with 100 ml methanol. The

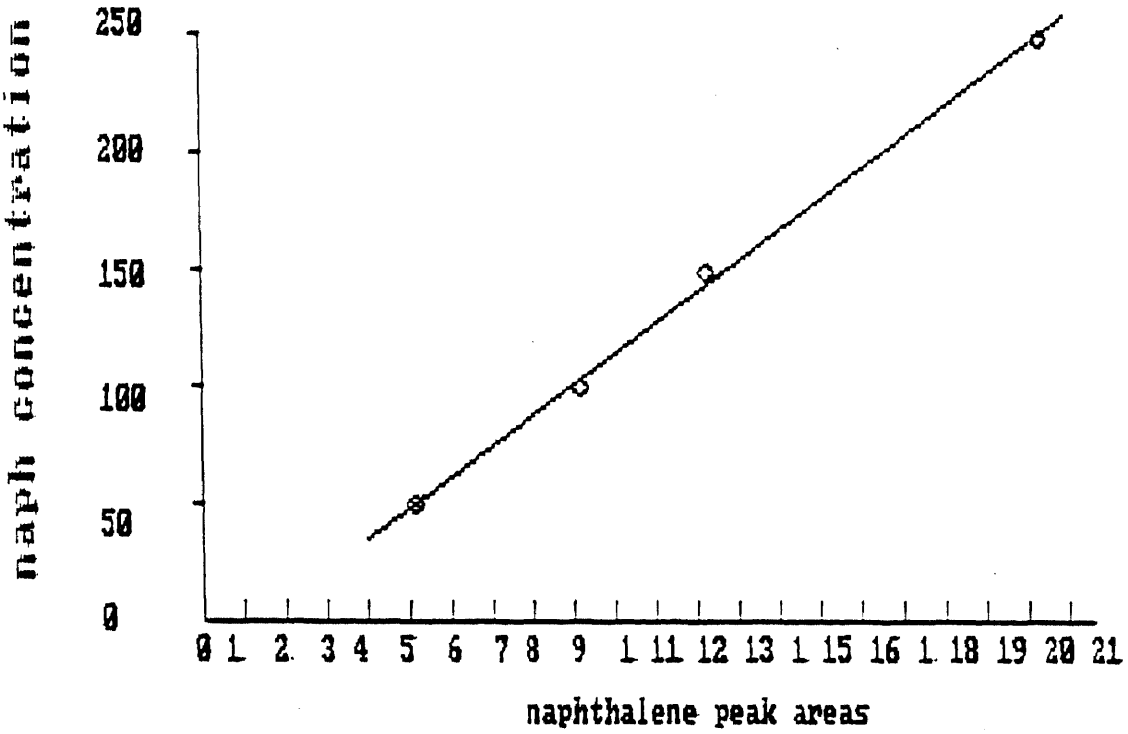


Figure 6-1: Average of Standard Peak Areas

expected concentration of naphthalene after extraction should be :

$$\frac{0.015 \text{ g naphthalene}}{79.14 \text{ g methanol}} = \frac{x}{10E6}$$

x = 189 ppm

15 ml 1000 ppm naphthalene solution are mixed with 30 g soil; the solvent is allowed to evaporate. The Soxhlet method is used for extracting naphthalene. 100 ml of methanol for 24 hours were used for the extraction.

Result: The extracting solution is diluted to 100 ml. 4 ul is injected into GC. The concentration of naphthalene is 170 ppm. This experiment shows that 90% of expected naphthalene concentration (170 ppm/189 ppm) can be extracted by Soxhlet method.

2). Experiments 1-3: The Effect of Varying the Concentration of Contaminants

In experiments 1-3, the soil with three different contaminat concentrations, 500, 250, 150 ppm, respectively, are treated by microwave for 3 minutes in a 200 ml beaker; then, the soil is extracted by Soxhlet. The results are as follows:

Table 1. Comparison of Different Soil Concentrations

#	soil (g)	naphth conc.	H2O add	MW min	meth. used	expect conc.	result conc.	naphth recover	naphth decrease
1	30	500ppm	/	3	100ml	189ppm	66ppm	34%	66%
2	30	250ppm	/	3	100ml	94ppm	33ppm	35%	65%
3	30	150ppm	/	3	100ml	56ppm	20ppm	36%	64%

(See also Figure 6-2: Comparison of Different Soil Concentrations)

Experiments 1-3 show that, with the same exposure time to the microwave energy, the degree of naphthalene concentration decreasing are nearly the same.

3). Experiments 4-7: Times of Microwave Treatment Varies

In experiment 4-7, the soil samples with 500 ppm naphthalene in a 200 ml beaker are irradiated with microwave energy for four different times. Then, soil samples are extracted by Soxhlet. The results are as follows:

Table 2. Comparison of Different Treatment Times

#	soil (g)	naphth conc.	H2O add	MW min	meth. used	expect conc.	result conc.	naphth recover	naphth. decrease
4	30	500ppm	/	3	100ml	189ppm	66ppm	34%	66%
5	30	500ppm	/	5	100ml	189ppm	30ppm	16%	84%
6	30	500ppm	/	7	100ml	189ppm	26ppm	13%	87%
7	30	500ppm	/	10	100ml	189ppm	21ppm	11%	89%

(See also Figure 6-3:Comparison of Different Treatment Time)

Expriments 4-7 show that the longer time of the microwave treatment, the less naphthalene can be recovered.

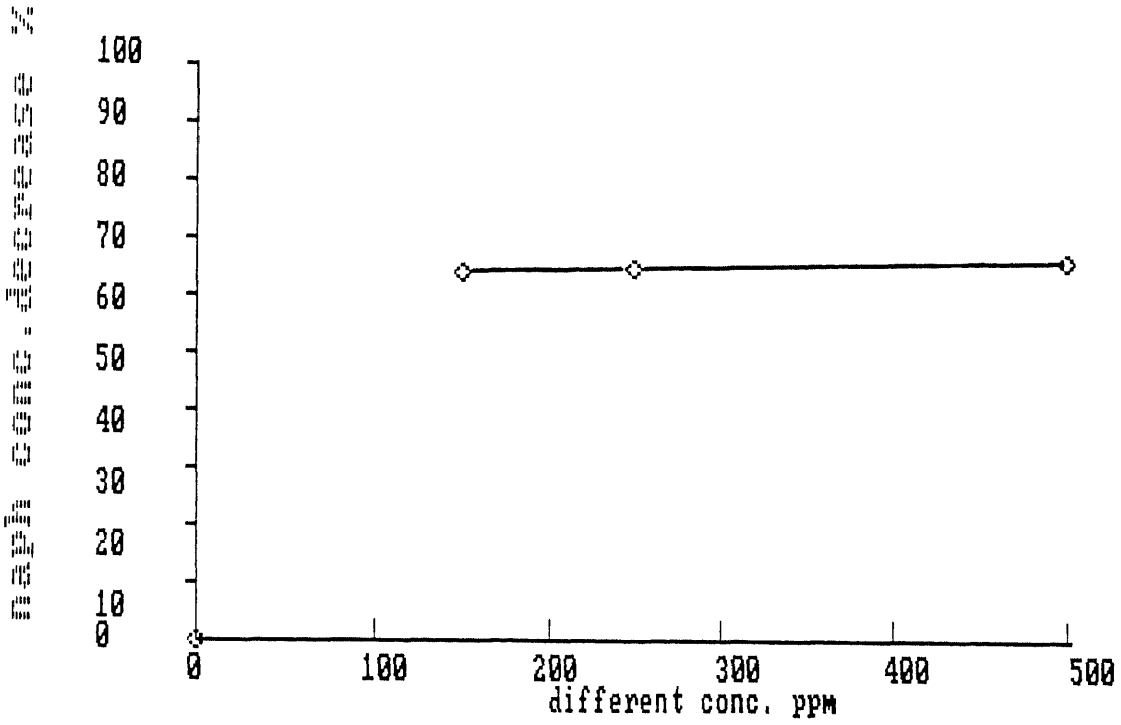


Figure 6-2: Comparison of Different Soil Concentrations

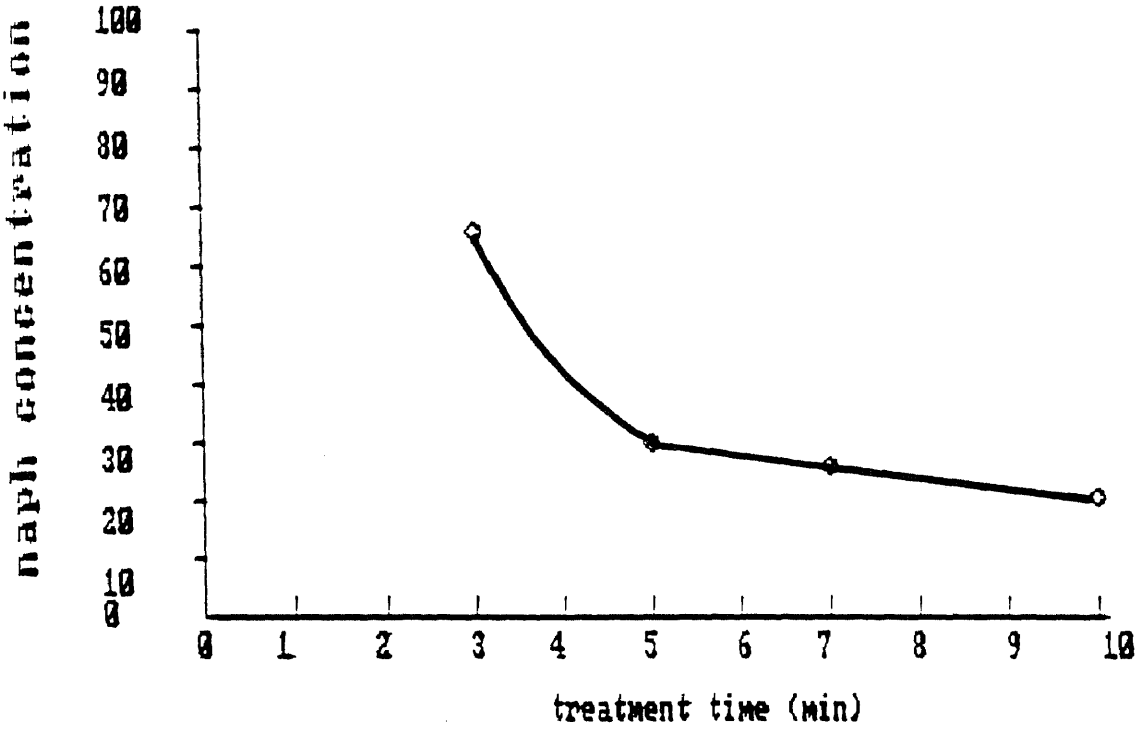


Figure 6-3: Comparison of Different Treatment Time

The concentration of naphthalene decreases with the increasing irradiation time. It is notised that, after the first 3 minutes, the naphthalene concentration decreasing is the maximum, about 66%. But, from 3 minutes to 5 minutes (2 minutes addition), naphthalene concentration decrease only 18% ; from 5 minutes to 7 minutes, naphthalene concentration decrease 3%; from 7 minutes to 10 minutes, naphthalene concentration decreases 2%. An explanation for this phenomenon is that water is needed to effect the removal of naphthalene from the soil. Although no water was added, the soil cantains about 19% water. After this water volatilized, then, the removal of naphthalene to form the ceases.

4). Steam Distillation

The microwave treatment is mainly based on the operation of steam distillation, which is effected batchwise in the chemical industry by the direct introduction of steam into the substrate to be treated. During this standard chemical industry unit operation, the separation of low volatile organics from the contaminated soil occurs. Steam distillation is achieved by the irradiating the contaminated substrate with electromagnetic energy of frequency 2,450 MHz. Water in this system is selectively heated (dipole molecules) heat is transferred to the non-absorbing organicsuntil the temperature is reached that is needed to effect a stam distillation.

Naphthalene, just like many commonly encountered

organic compounds, is immiscible with water. When two immiscible substance, such as naphthalene and water, are heated together, each will exert its own vapor pressure independently of each other. The total vapor pressure above the two-phase mixture is equal to the sum of the vapor pressures of the pure components at that temperature. Assuming that the atmospheric pressure is 760 mmHg, the mixture will boil at 86°C, because at 86°C

P^{o} nap = 10 mmHg

P^{o} water = 750 mmHg

P^{o} nap + P^{o} water = 760 mmHg

therefore, a mixture of naphthalene and water distill at 86°C.

An ideal gas law calculation shows that the mole fraction of naphthalene in the distillation head is 0.013 (10/760). The mole fraction of the water in the vapor is 0.98 (750/760). Since naphthalene has a much higher molecular weight (128.17) than water (18), its weight percentage in the vapor will be greater than 0.013. On a weight basis, the ratio of naphthalene and water is 10 mmHg x 128.17 (mol. wt of nap.) = 1281.7 g of the naphthalene to 750 mmHg x 18 (mol.wt of water) = 13500 g of the water, or, the two compounds distill in a weight ratio of 1 part of naphthalene to 10.5 parts of water. This favorable ratio (because only small amount of water is needed) is possible, of course, only if the organic compound has a relatively high molecular weight and a vapor pressure of at least 10-20 mmHg at 100°C (The vapor pressure of naphthalene at 100°C

is 20 mmHg).

Water also has several characteristics which make it a favorable choice: it is available, inexpensive, and of low molecular weight. Because of its low molecular weight, a large number of moles of water can be distilled over even though the volume of water will not be great (see exp.9-11).

A major advantage of steam distillation is that even a high boiling compound, like naphthalene, which decomposed at or near their boiling point, can be steam distilled at a temperature low enough to prevent decomposition. For example, naphthalene boiling point is 218.87^{o}C; in steam distillation it will boil at 86^{o}C. Then, condenser can be used to collect naphthalene or recycle it, so that, microwave decontamination technology would not cause the pollution in other area during its operation.

In experiments 8-11, different amounts of water are added to soil samples in the 200 ml beaker. The times of microwave treatment are the same (3 minutes).

Table 3. The Effect of Steam Distillation

#	soil (g)	napth. conc.	H2O add	MW min	meth. used	expe . conc.	result conc.	naphth recover	naphth. decrease
8	30	500ppm	/	3	100ml	189ppm	66ppm	34%	66%
9	30	500ppm	1ml	3	100ml	189ppm	9.2ppm	5.8%	94.2%
10	30	500ppm	5ml	3	100ml	189ppm	<2ppm	1.2%	98.8%
11	30	500ppm	10"	3	100ml	189ppm	/	0%	100%

(See also Figure 6-4: The Effect of Steam Distillation)

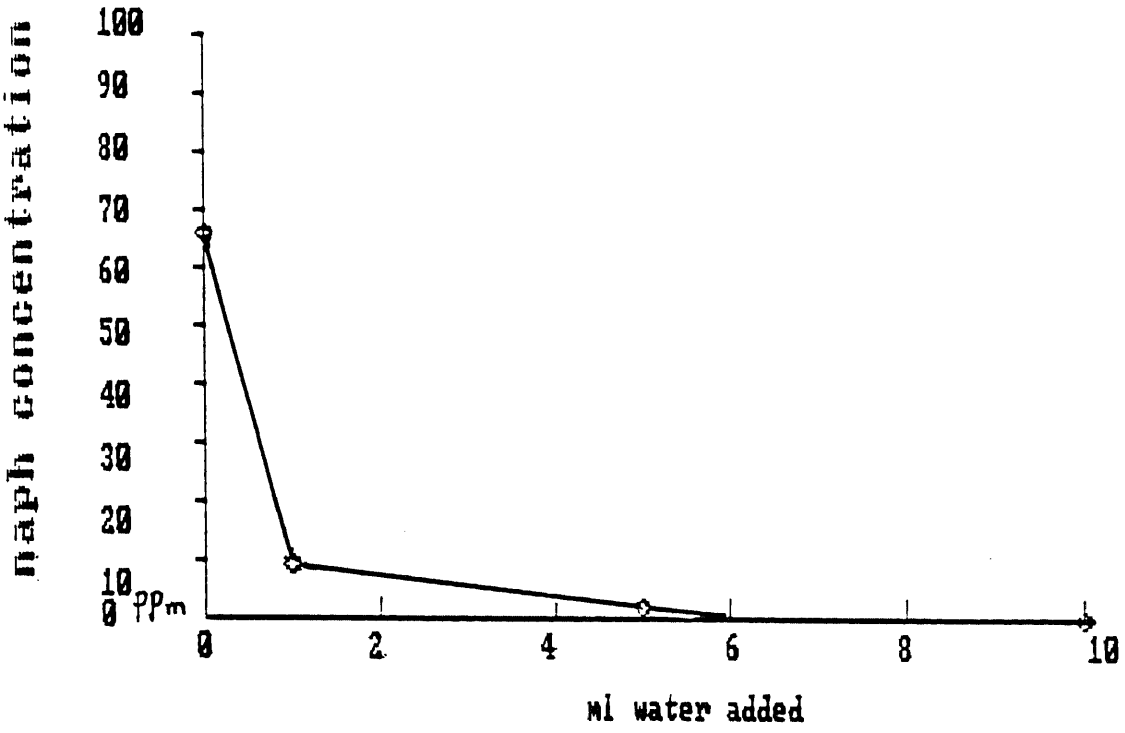


Figure 6-4: The Effect of Steam Distillation

It is noticed that steam distillation is such an efficient method: only 10 ml water is added to reach the 99.999% efficiency.

5). The Penetration of Microwave Energy

Batchscale experiments have shown that steam distillation effected by microwave radiation causes the volatilization of naphthalene from soil. To determine the feasibility of utilizing the process on an industrial scale, it must be studied on an intermediate scale of operations which is called the pilot plant scale. The soil will processed continuously as it moves on a conveyor belt through the microwave cavity. An important operational parameter is the depth of the soil to be placed on the conveyor. That depth should be the maximum which the microwave energy can penetrate to assure decontamination of all the soil. To determine how deep the layer of soil should be on the conveyor belt in the pilot plant operation is the goal of this study.

In experiments 12-14, the depth of microwave radiation penetration is measured. All of the soil samples are placed in 100ml beakers, which are surrounded by the foil paper with only the top of the beakers exposed to radiation.

The results are showed as follows:

Table 4. The Depth of Penetration

#	Soil g	naph. conc.	H2O add	MW Min	soil height	total layer	Naph left in soil layer 1	layer 2	layer 3
12	90	500ppm	/	5	1 in	2	23ppm	33ppm	
13	90	500ppm	/	5	1.5 in	3	11.5ppm	19ppm	43ppm
14	90	300ppm	/	5	1.5 in	3	< 2ppm	<2ppm	14ppm

From the three experiments, it is postulated that the naphthalene concentration decrease reaches the maximum in the first layers which are about 0.5 inch. At a depth of 1 inch, decontamination can still be effected. The theory of microwave penetration is that, as microwave energy enters a material, the energy density at the surface is usually the greatest and its energy density falls off exponentially because as the microwave penetrate deeper into the material, energy is absorbed by the moisture in the soil. The above results refer to experiments in which no water was added. These depths should increase greatly when water is added to the soil. Howere, this effect can not be predicted. It must be determined directly in the pilot plant studies.

From experiments 12-14, it can be concluded tnat the efficient depth of microwave penetration is about 1 inch in this experiment.

6) Sand Study

Sand is not dielectron material and it does not absorb microwave energy. But sand study show that sand greatly

enhance the effect of microwave decontamination.

In experiments 15 to 18, 500 ppm naphthalene contaminated soil samples are placed in a tubes, and each tube is surrounded by sand in a 200 ml beaker. They are exposed to microwave energy in different times.

The results are shown as the follows:

Table 5: Sand around the soil samples

soil g	Naph Conc.	MW min.	Rslt Conc.	naph recover	naph.Dec.
30	500 ppm	3	33 ppm	17%	83%
30	500 ppm	5	16 ppm	8.4%	91.6%
30	500 ppm	7	13 ppm	6.8%	93.2%
30	500 ppm	10	< 2 ppm	1%	99 %

(See also Figure 6-5: The Effect with Sand Around Sample)

In experiments 19 to 22, 500 ppm naphthalene contaminated soil samples are placed in the top of sand in the 200 ml beakers. The times of exposure to microwave energy are different.

The results are shown as follows:

Table 6: Soil samples on the top of sand

soil g	Naphth Conc.	MW Min	Rslt Conc.	naph recover	Naph Dec.
30	500 ppm	3	52 ppm	27%	73%
30	500 ppm	5	41 ppm	21%	79%
30	500 ppm	7	16.8 ppm	8.8%	91.2%
30	500 ppm	10	< 2 ppm	1%	99%

(See also Figure 6-6: Effect with Sample on Top of Sand)

By comparing the results from sand-around and on-top-of the-sand samples, it can be found that microwave treatment

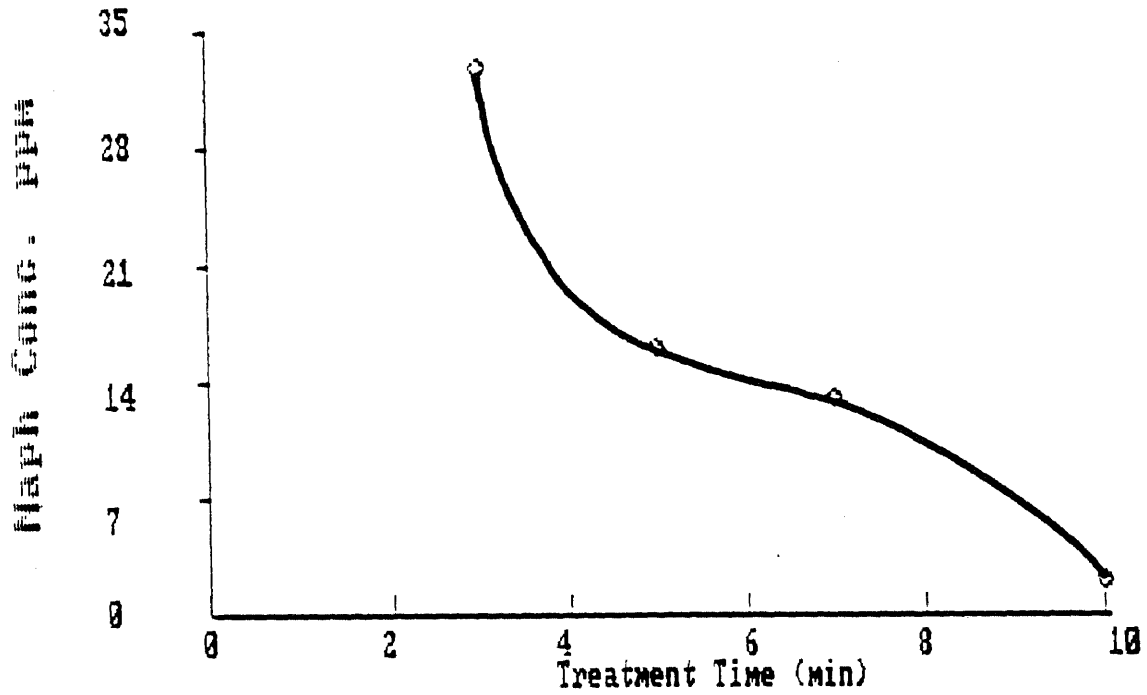


Figure 6-5: The Effect with Sand Around Sample

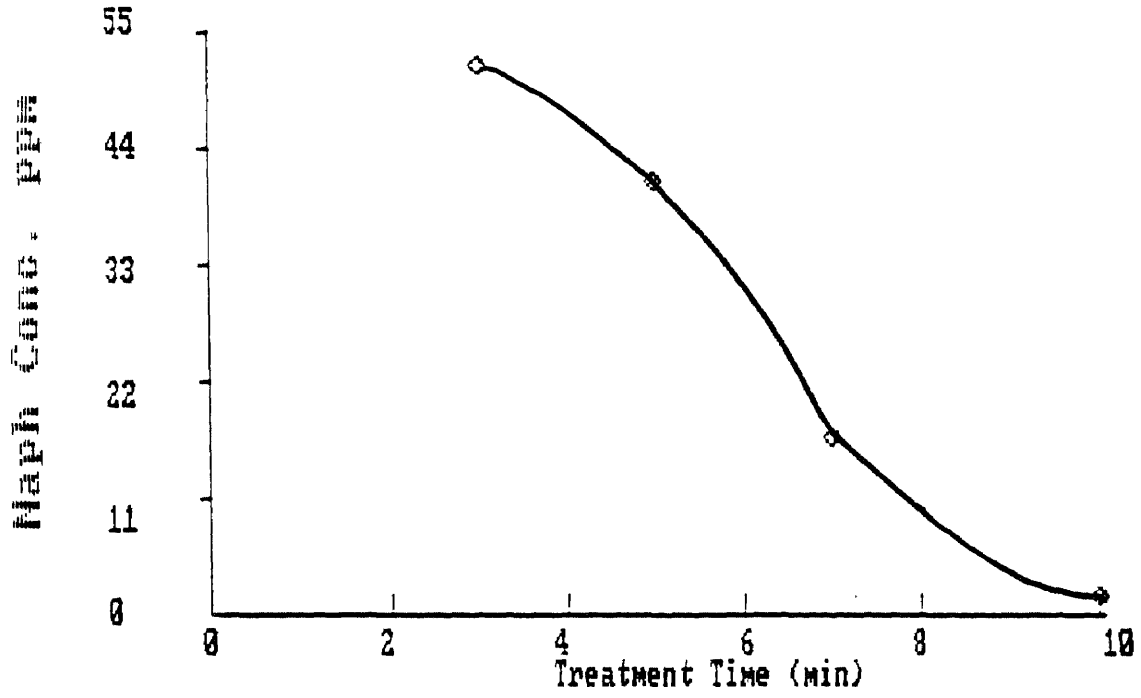


Figure 6-6: Effect with Sample on Top of Sand

is more efficient on sand-around sample than on sample on top of the sand in the first 7 minutes, and when microwave treatment reaches 10 minutes, both results are the same (less than 2 ppm). The reason for thit is, when microwave energy transmitted from glass beaker to the sand, the heat accumulated in sand. Sand is an insulator and will heat up rapidly because it is not a conductor and cannot conduct heat out of itself. Then the temperature increases rapidly inside sand. By contacting with sand in the beaker, soil samples are heated by both microwave energy from the top and the sand from either the beside or the bottom. Because the soil samples which are around by sand, have more surface areas contact with sand so that the naphthalene concentration decrease fast than the samples which are on the top of the sand. But as long as the time for microwave treatment increasing, the both methods can reach the same efficiency.

3. CONCLUSION OF NAPHTHALENE STUDY

Table 7: Conclusion of Microwave Treatment Methods

# EP	soil g	Naphth conc.	H_2O add	Sand top/ard	MW min	result conc.	naphth recover	Naphth decrease
1	30	500ppm	/	/	3	66ppm	34%	66%
19	30	500ppm	/	top	3	52ppm	27%	73%
15	30	500ppm	/	around	3	33ppm	17%	83%
11	30	500ppm	10ml	/	3	o	o%	99.999%

The above table summarizes the results of experiments using different microwave treatment methods.

The conclusion for naphthalene study is that naphthalene can be steam distilled. It is inferred that, in general, relatively non-volatile organics can be removed from soil by steam distillation. The depth of penetration studies are inconclusive but suggest methods that should be used in the pilot plant level. Also, surrounding the contaminated soil with sand appears to be a way to make the process more cost effective.

CHAPTER 7 TCE Study

A. APPROACH OF THIS STUDY

Trichloroethylene (TCE) is a liquid organic chemical,and has high vapor pressure at room temperature. The goal of this study is to evaluate the microwave treatment to the volatile chemicals.

B. EXPERIMENTAL

1. Preparation of TCE Standards

1). TCE Standard Solutions

Methanol is used as a solvent for preparation of TCE solutions because TCE and methanol solution has very well separated peaks in GC.

1000 ppm TCE solution :

0.1 ml 99.99% TCE is taken and diluted to 100 ml with methanol. The calculation is as follows:

$$\frac{0.1 \text{ ml pure TCE}}{100 \text{ ml methanol}} = \frac{X}{10E6}$$

X = 1000 ppm

150 ppm TCE solution:

15 ml TCE is taken from 1000 ppm TCE solution:

$$\frac{\text{15 ml TCE}}{\text{100 ml Methanol}} = \frac{\text{X}}{\text{1000 ppm}}$$

X = 150 ppm

100 ppm TCE solution:

10 ml TCE is taken from 1000 ppm TCE solution:

$$\frac{\text{10 ml TCE}}{\text{100 ml Methanol}} = \frac{\text{X}}{\text{1000 ppm}}$$

X = 100 ppm

50 ppm TCE solution:

5 ml TCE is taken from 1000 ppm TCE solution:

$$\frac{\text{5 ml TCE}}{\text{100 ml Methanol}} = \frac{\text{X}}{\text{1000 ppm}}$$

X = 50 ppm

2). GC (series 580) Standard Conditions for TCE Peaks

This study was carried out at the conditions of GC listed below:

Attenuation	Range :	16 x 10E-11
Temperature:	Detector:	200°C
	Injection:	100°C
	Column:	50°C
Flow rate:	Helium :	120ml/min
	Air :	30ml/min
	H2:	20ml/min

3). Standard TCE Peak Areas

The TCE peak areas are as follows:

Concentration of TCE ppm	Peak areas
50	1.12 x 10E-10
100	2.688 x 10E-10
150	4.608 x 10E-10

(See also Figure 7-1: Standard TCE Peak Areas)

From concentration and peak area calibration with regression analysis get linear relationship as follows:

a = 20.8525
b = 28.2580
r2= 0.9818

The concentration calculation is:

Concentration of TCE = a + b x TCE peak area

4). Calculation of 500 ppm TCE in 30g Soil.

The weight of TCE needed for 500 ppm TCE in 30g soil is calculated as follows:

$$\frac{X \text{ g TCE}}{30 \text{ g soil}} = \frac{500 \text{ g TCE}}{10E6 \text{ g soil}}$$

X = 0.015 g = 15 mg

Since 1 ml 1000 ppm TCE solution has 0.001 ml 99% TCE, and the density of TCE is 1.46 mg, therefore, 10 ml TCE

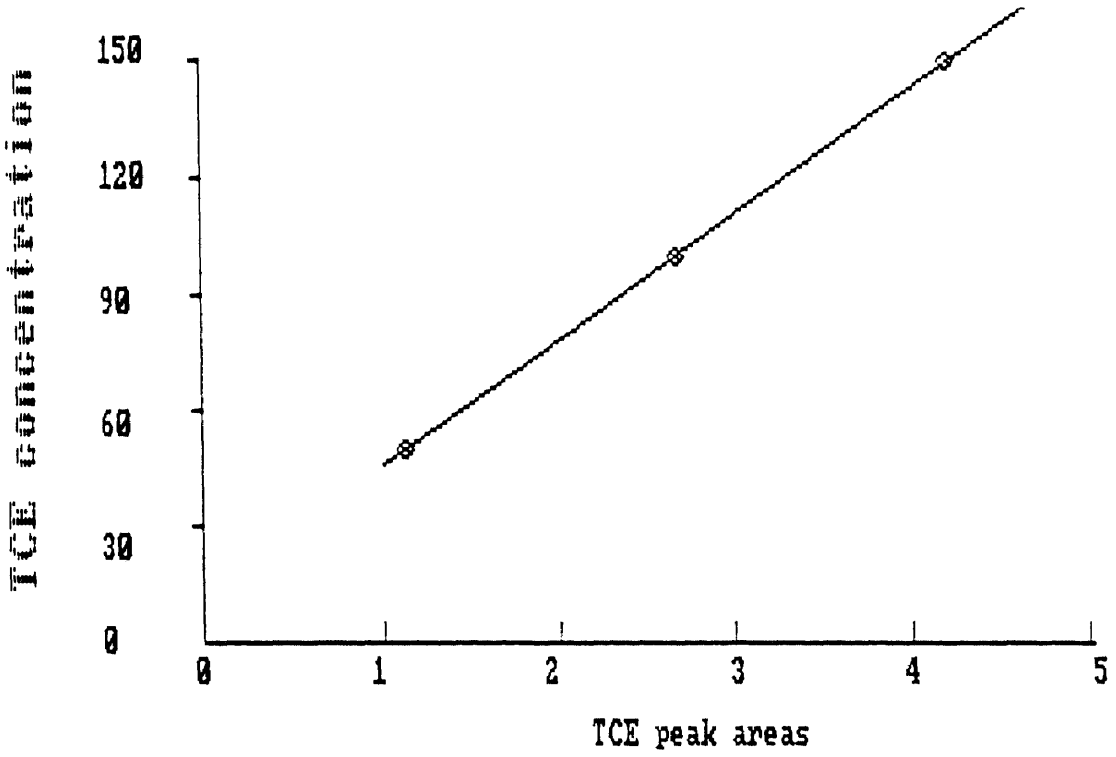


Figure 7-1: Standard TCE Peak Areas

1000 ppm TCE solution is needed for 15 mg TCE, the calculation is as follow:

$$\frac{\text{15 mg TCE}}{\text{1.4642 mg TCE}} = \text{10 ml 1000 ppm TCE solution}$$

5). The Expected TCE Concentration after Extraction from Soil

10 ml 1000 ppm TCE will be extracted by 100 ml methanol for analysis. The concentration of TCE in extract of methanol can be calculated as follows:

$$\frac{\text{0.015 g TCE}}{\text{95.75 g methanol}} = \frac{X}{\text{10E6 g}}$$

$$X = 156 \text{ ppm}$$

156 ppm TCE is the expected concentration from extraction.

2. Experiments With Soxhlet Extraction

1). Experiments 1-6

In experiments of 1 to 6, 30 g soil is mixed with 10 ml 1000 ppm TCE solution, and extracted with 100 ml methanol using Soxhlet extractor. After extraction, the extract solution is diluted to 100 ml by methanol and 4 ul is injected into GC.

In experiments 1 and 6, the methanol in the TCE solution which is mixed with soil is allowed to evaporate to dryness. In experiment 4, dry ice is used in condenser so that the temperature in condenser is lower than the temperature with cold water. In experiment 5, the glass thimble is used instead of the cellulose thimble in order to prevent TCE adsorption by the cellulose thimble. The results are as follows:

Table 1: Experiments 1-6

#	soil g	TCE conc.	soil cond.	methan. used ml	extra. time h	thimble cond.	condenser used	TCE found
1	30	500ppm	dry	100	2.30	dry	cold H_2O	0
2	30	500ppm	wet	100	2.30	dry	cold H_2O	0
3	30	500ppm	wet	100	24	wet	cold H_2O	82ppm
4	30	500ppm	wet	100	2.30	wet	dry ice	45ppm
5	30	500ppm	wet	150	24	glass	cold H_2O	0
6	30	500ppm	dry	100	24	wet	cold H_2O	0

It is noticed from experiments 1 and 6 that TCE was not able to be extracted from dry soil sample.

2). Experiment 7

In experiment 7, a soil sample was put into a glass thimble with a coarse frilled disk which has a very good permeability. The bottom flask was filled with 150 ml methanol. The condenser is run with cold water; extraction time is 48 hours.

After 24 hours of extract time by Soxhlet, 4 ul sample solution is taken from flask and injected into GC. The Soxhlet extraction still continuing. Trace of TCE was detected but the TCE concentration can not be measured by GC.

At the same time, 4 ul solution was taken from the Soxhlet apparatus and injected into GC. The TCE peak area is 1.296 x 10E-10; the concentration of TCE is 57.4 ppm.

After 48 hours, 4 ul solution is taken from flask and injected into GC. No TCE peak was detected by GC.

At the same time, 4 ul solution is taken from Soxhlet apparatus and injected into GC. The TCE peak area is 1.024 x 10E-10, the concentration of TCE is 49.78 ppm.

Table 2. Experiment 7

extraction Time	solution taken	TCE Found
24 Hours	flask	0
24 Hours	apparatus	57.4ppm
48 Hours	flask	0
48 Hours	apparatus	49. 78ppm

3). Conclusions of Experiments 1 to 7

(1). The TCE concentration can not be detected by GC from dry soil samples neither after two and half hours nor 24 hours extraction time and regardless the extraction methods (see experiments 1, 6).

(2). The TCE concentration can not be detected by GC from wet contaminated soil samples after two and half hours extraction because the time is short, except when dry ice is used even samples are immediately extracted after mixed with TCE (see experiments 2).

(3). When dry ice is used to decrease the temperature f condenser, TCE concentration is detected by GC from the wet soil sample even though extraction time is only two and half hours (see experiment 4).

(4). When wet soil was extracted immediately after being contaminated with TCE for 24 hours, the TCE concentration is detected by GC (see experiment 3).

(5). TCE concentration can not be detected by GC by using poor permeability glass thimble because of over flow of solution. Even if the glass thimble has good permeability, after 24 hours extraction, the TCE peak is still to small to be measured by GC (see experiment 5).

(6). When TCE concentration can not be detected by GC from flask solution, it can be detected by GC from soxhlet apparatus solution (see experiment 7).

(7). The results obtained with 24 hours extraction are not different from the results obtained with 48 hours extraction (see experiment 7).

4). Analysis and Discussion of Experiments 1 to 7

(1). TCE solution composed of both TCE and methanol will boil at the temperature between the boiling point of TCE

($87^{o}C$) and methanol boiling point ($65^{o}C$), assuming they form an ideal solution. The boiling point of a mixture is a function of vapor pressures of the various components in the mixture. According the Raoult's law, the vapor pressure exerted by methanol P will be equal to only a fraction of the vapor pressure (P^{o}) of pure methanol at the same temperature, where X is the fraction of molecules of methanol in solution, called the mole fraction of methanol.

P methanol = P^{o} methanol x X methanol

the same is true for TCE:

P TCE = P^{o} TCE x X TCE

At room temperature of $25^{o}C$, the methanol vapor pressure is 100 mmHg; its fraction of molecule is calculated as follow:

Mole of Methanol = 100 ml (0.87 g/ml D)/ 32 g (Wt)

= 2.718 mole

Mole of TCE = 0.01 ml (1.47 g/ml D)/131 g (Wt)

= 1.122 x 10E-4 mole

Total mole = 2.7181122

X methanol is 0. 99; and X TCE is 4.1278 x 10E-5

P methanol = 0.99 x 100 mm = 99 mm

P TCE = 4.1278 x 10E-5 x 77 mm = 3.178 x 10E-3

P total = PM + PT = 99 mm + 3.178 x 10E-3

= 99.005 mmHg

At boiling point of both TCE and methanol, the total vapor pressure is equal to 760 mm. Since methanol vapor

pressure at 59.3^{o}C is 99.95% of the mixture's vapor pressure, its vapor pressure is 752.4 mm, and TCE vapor pressure is 0.05% of this mixture's vapor pressure. At 59.3^{o}C, TCE vapor pressure is 3.6 mm. This boiling temperature is below the ideal TCE and methanol solution boiling temperature of 76^{o}C; it is not an ideal solution. It can be concluded from above calculations that the loss of TCE during the extraction is very small.

(2).When the temperature of condenser is decreased by dry ice, TCE concentration is detected by GC in extraction time of two and half hours because of the decreasing of the rate of evaporation of TCE though the mouth of condenser. But the concentration of TCE detected by GC is only 28% of the expected concentration.

(3).At room temperature of 25^{o}C, TCE vapor pressure is 60 mmHg and methanol is 100 mmHg. It can be imagined that after soil is mixed with TCE solution and kept in hood until it is dry, most of TCE and methanol have gone. It is not possible to extract a measurable amount of TCE from the dry soil regardless the extraction time.

(4).The TCE Koc (octanol/water partition coefficients) is 126 ml/g. Organic contaminants that have a high Koc value, therefore, they would be expected to be tightly bound to the soil. The Koc of TCE is not high, but it still tends to be bond with soil. This is another reason that it

is difficult to extract TCE.

5). Experiments 8 to 10

It is postulated from experiments 1-7 that most of TCE is evaporated when soil is dried in the hood; and a smaller part of the loss is due to the extraction because the solution is heated to boiling. In experiments 8-10, the temperature of the solution is set low enough to keep it from boiling during the extraction time to minimize the loss from extraction.

In experiments 8 and 9, the soil samples are mixed with 10 ml 1000 ppm TCE solution, kept them under the hood until dryness. The extraction times were two and half hours and 24 hours respectively, but in neither extraction was TCE detected.

In experiment 10, the dry soil sample is changed to the wet soil sample. After the soil sample is mixed with 10 ml 1000 ppm TCE solution, the extraction began immediately. Extraction times are 2.30 h and 24 h. During the extraction time, TCE solution is not boiled. The methanol used for extraction is 50 ml, and the expected concentration is 287 ppm. The results of the average of three injections from this experiment are as the follows:

Table 5-1, Experiment 10

Extract Time	Expected Conc	Result Conc.	TCE Recovered
2.30 h	287 ppm	45 ppm	15%
24 h	287 ppm	62 ppm	21%

6). Conclusion and Discussion on Experiments 8,9,10

In experiments 8 and 9, no TCE concentration is detected by GC since the soil samples are dry. In experiment 10, TCE concentration is detected by GC in two and half hours and twenty four hours extraction. After extraction temperature is decreased, the evaporation of methanol and TCE during the extraction is obviously decreased. Unfortunately, the TCE concentration still cannot be extracted from dry soil samples.

3. Experiments From the Soil Using Aqitation to Extract TCE

The preferred method of analysis is by the Soxhlet process because the procedure is based upon continuous equilibrium stage extraction. This should lead to optimum extraction. But practical difficulties as discussed above have led us to conclude that it cannot be effected. The alternate procedure, aqitation, which is a single stage equilibrium process, was then tried. It is to be noted that although aqitation is the procedure recommended in the EPA protocols for the testing of TCE-contaminated soils, such protocols represent standard procedures but do not successfully effect complete extraction of the TCE. This problem is overcome in the protocols by the use of surrogates. The extractability of the contaminant is ratioed to the extractability of the surrogate. But in these studies on the microwave treatment, the most meaningful results

would be those based on the absolute amount of TCE destroyed.

1). Experiments: Manual Agitation

In the experiments of shaking by hand, the soil samples are prepared with 10 ml 1000 ppm TCE solution also. Then, soil samples are shaken in a flask by using 100 ml methanol. The cellulose thimble are used for filtering after shaking. No TCE concentration is founded after shaking. The results are showed below:

Table 6. Experiments of Hand Shaking

Soil g	TCE conc.	soil cond.	shaking T	TCE Found
30	500 ppm	dryness	10 min	0
30	500 ppm	dryness	30 min	0

2). Ultrasonic Agitation:

In the experiments using ultrasonic, the soil samples are also mixed with 10 ml of 1000 ppm TCE solution, and 100 ml methanol is used for extraction. The cellulose thimble is used for filtering. The results are shown as the follows:

Table 7. Experiment of Ultrasonic Shaking

soil g	TCE conc.	soil cond.	shaking T	TCE Found
30	500 ppm	dryness	5 min	0
30	500 ppm	dryness	10 min	0
30	500 ppm	dryness	20 min	0

The conclusion from these results is that extraction can't be effected by ultrasonic agitation. But the scope of the experiments limits, namely, the conclusion is dependent upon the filtering procedure. During filtering losses may have occurred because the filtering time was too long and the mixture tended to agglomerate.

4. Analysis of TCE Concentration By GC/MS (HP 5890,5970)

GC/MS has high sensitivity than GC. In order to detect the TCE concentration in soil samples after extractions, GC/MS is used for analysis the results. The results from GC/MS are showed as follows:

Table 8, Experiments with GC/MS

soil g	TCE conc	soil cond	method Used	shaking T	TCE Found
30	500ppm	wet	Ultrasonic	5min	50 ppm
30	500ppm	dryness	ultrasonic	5min	< 10ppm
30	500ppm	wet	hand shak	30min	50ppm
30	500ppm	dryness	hand shak	30min	< 10ppm
30	500ppm	wet	soxhlet	2.3 h	25 ppm
30	500ppm	dryness	soxhlet	2.3 h	0

It is clear that the measurable concentration of TCE after soil is dry is less than 10 ppm. Comparing the results from the above table, the best method for extracting TCE is ultrasonic, since it takes less time and produces better results.

5. Conclusions Of TCE Study

In the TCE study, more than 20 experiments have been done to determine the extractive of TCE from soil which is contaminated with the known amount of TCE. The conclusion from those experiments is that after soil is contaminated by TCE for more than 2 hours (the contamination concentration of TCE is below 500 ppm since extraction solvent has diluted the concentration), the meaasurable concentration of TCE in soil sample is less than 10 ppm. The concentration of TCE in soil decreases fast when it is evaporating at room temperature. Since TCE concentration in contaminated soil is too low to be detected by GC due to its fast evaporation, microwave treatment study on TCE can not be conducted.

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